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6. AUTHOR(S)

Gerald Roberts
Eva Maya
Arthur Snow
James Shirk

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

George Mason University
4400 University Drive, Fairfax, VA 22030
Naval Research Laboratory
4555 Overlook Ave. SW, Washington, DC 20375

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14. ABSTRACT

This final report summarizes research on the synthesis, character-ization and evaluation of phthalocyanine and phenanthralocyanine compounds with peripheral siloxane substitution. These materials are intrinsic liquids, have very low degrees of dye aggregation and significant merit for the optical limiting application. The phthalocyanine is better qualified than the phenanthralocyanine for this application.

15. SUBJECT TERMS

Optical limiting, Phthalocyanine, silicone, siloxane, Phenanthralocyanine, Nonlinear Optical Materials

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Advanced Optical Limiter Materials: Final Report

Contents

I. Introduction

Optical limiters are nonlinear optical devices whose transmission decreases with increasing applied intensity. These devices require materials with appropriate nonlinear optical response mechanisms, in particular nonlinear absorption and nonlinear refraction. The nonlinear absorption properties of many dyes have been investigated. It has been found that materials that have higher absorption cross sections in the excited state than they do in their ground state yield positive nonlinear absorption coefficients. This effect is sometimes called reverse saturable absorption (RSA). A number of dye materials, primarily phthalocyanines and porphyrins, with large positive nonlinear absorption coefficients have been reported. The desirability of materials with a large intensity or fluence dependent refractive index in such applications has been recognized. We know of few examples of materials that are strong nonlinear absorbers and also possess a large nonlinear refractive index. In most previous cases the refractive response was dominated by that of the solvent. An intrinsic, fluence dependent refractive index is desirable when the nonlinear material is used pure as a thin film.

The peripherally substituted silicone phthalocyanines (Pc's) reported here combine large nonlinear absorption and nonlinear refraction coefficients. The source of the fluence dependence of the refractive index is thermal. Our hypothesis is that the silicone-substituted phthalocyanines can couple the large refractive index variation with temperature (dn/dT) characteristic of the siloxane structure with the large nonlinear absorption (reverse saturable absorption) characteristic of the phthalocyanine ring.

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In addition to the nonlinear response characteristics, these silicone phthalocyanines possess other useful properties: optical transparency over a relatively broad region, photo-oxidative stability, as evidenced by the invariance of the UV-vis absorption over a period of months, and processability as a solution, glass or liquid. In previous materials, some of these properties have been achieved. Peripheral substitution of arylethers at the phthalocyanine ring, for example introduction of cumylphenoxy substituents, generates effective optical limiting materials with excellent solubility and photo-oxidative stability. However, this material is a solid in pure form and does not readily form transparent films. The introduction of an alternative peripheral substituent group, phenylglycidylether, allowed the formation of optically clear thin films of the pure material. These thin films are glassy and were found to have relatively low damage thresholds. Attachment of ethyleneoxide oligomer substituents to the Pc core, yields intrinsic liquids which also form optically clear films that have the ability to self heal if optically damaged. Unfortunately, the material with the best nonlinear absorption characteristics, a lead substituted version, was found to be unstable upon dilution in common solvents.

Another important feature in phthalocyanine design for nonlinear optical applications is the control over the aggregation. Phthalocyanines tend to form aggregates in solution and films. Aggregation reduces the excited state lifetime and hence the effective nonlinear optical absorption coefficients. Strategies to reduce aggregation include incorporation of long alkyl chains in the α-position of the phthalocyanine ring or substitution at the β position with bulky groups such as large dendritic substituents. We

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postulated that the substitution of the Pc ring with poly(dimethylsiloxane) chains (10 repeat units length) would also be effective for suppression of aggregation in solution.

II. Program Objectives and Goals

The overall goal of this work is to develop new materials that will reduce the threshold and increase the high fluence opacity of the optical limiters. The specific goal of this work is to synthesize materials with the physical and optical properties necessary to enable the fabrication of nonlinear photonic crystals, an entirely new class of nanostructured optical limiter materials. These nanostructured materials are expected to substantially enhance their optical limiting properties over those of homogeneous nonlinear materials. Specific accomplishments for this program are as follows: (1) Synthesis and characterization (including nonlinear optical measurements) of liquid polydimethylsiloxane substituted phthalocyanines; (2) Syntheses and characterization of a new extended ring phthalocyanine derivative (phenanthralocyanine) with peripheral siloxane and hydrocarbon substituents; (3) Preparation of homogeneous lead phthalocyanine / polycarbonate blends for fabrication of layered photonic band gap structures.

III. Approaches

a) Phthalocyanine System

For the oligodimethyloxane substituted phthalocyanine system the synthetic scheme illustrated below in Scheme I was followed.

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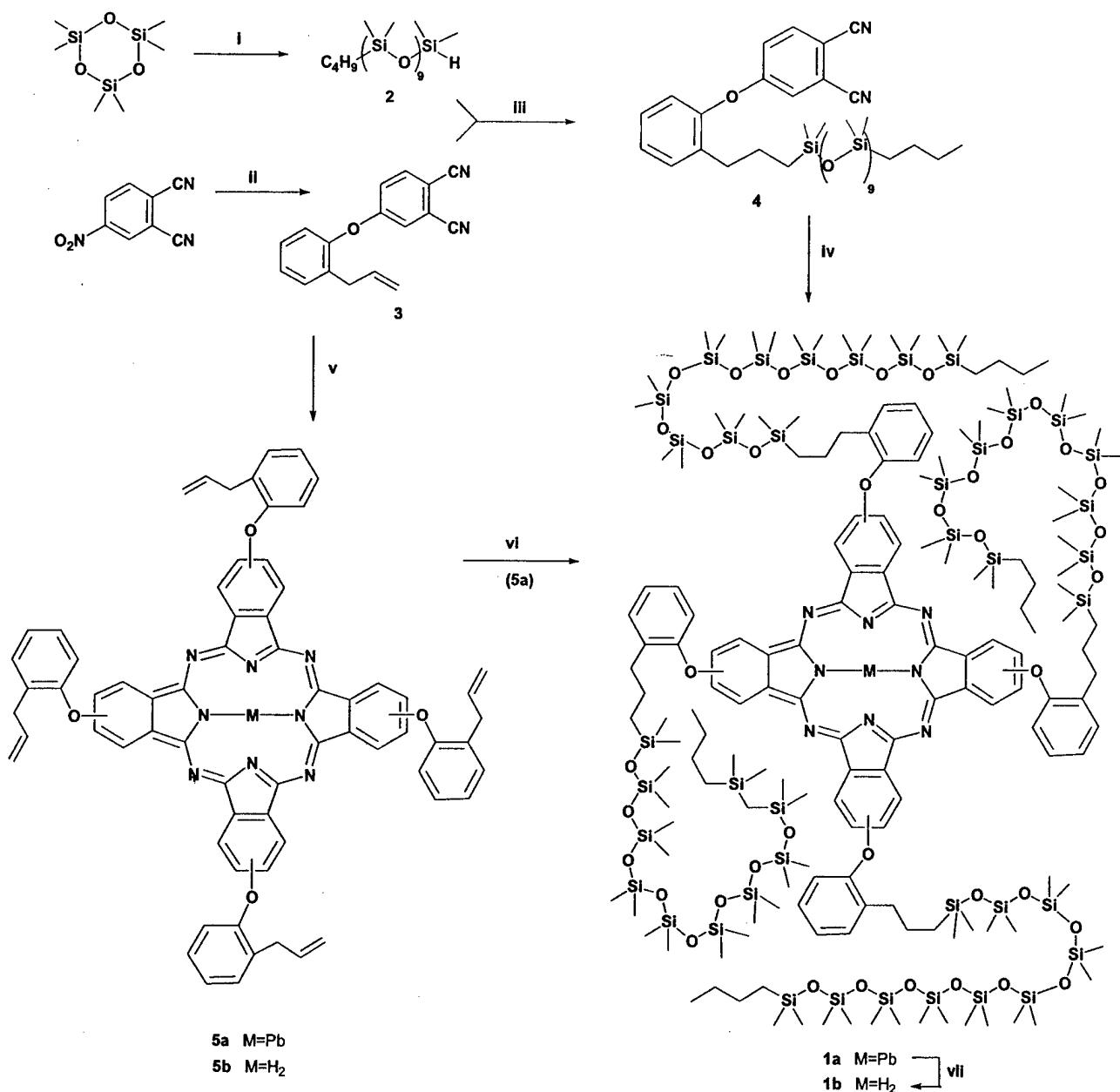
Scheme 1. Syntheses of liquid oligodimethylsiloxane phthalocyanines.

As illustrated above two complementary synthetic routes to the same product were undertaken with the finding that the one coresponding to iv being the superior. This

product was the first phthalocyanine compound found to be an isotropic liquid at room temperature. The viscosity of these liquids was low enough that short path length (~4 micron) optical cells could be filled by capillary action of the neat liquid. This allowed for significant nonlinear optical measurements to be made on the neat liquid material. This capillary action filling of the phthalocyanine liquid in to small spaces is also particularly useful for the fabrication of photonic band gap materials. The chain length of the oligodimethylsiloxane peripheral substituent was varied between 9 and 18 repeat units, and one of the methyl groups was substituted by a phenyl group.

b) Phenanthralocyanine System

The phenanthralocyanine synthesis was a much more high risk approach to phthalocyanine optical limiter materials in that the added benzannelation of eight rings incurred the risk of significant solubility imposed restrictions on purification and processing. However, theoretical studies indicated that significant benefit might be realized by a larger more highly conjugated and delocalized system as compared with the phthalocyanine system. Three substituents were chosen that were considered to be good candidates to induce solubility and liquidity in the phenanthralocyanine system: cumylphenoxy; nonylphenoxy; and the oligodimethylsiloxane. All of these substituents promoted good solubility and purification characteristics through the three step leading to the dicyanophenanthrene precursor to the phenanthralocyanine as depicted in Scheme 2, and all three precursors could be converted to the phenanthralocyanine as depicted in Scheme 3 below.
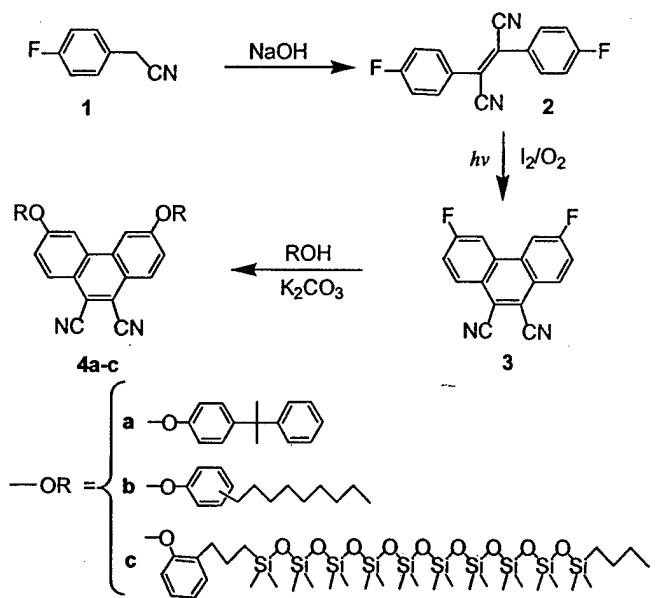
Scheme 2. Synthesis of various substituted 9,10-dicyanophenanthrenes.
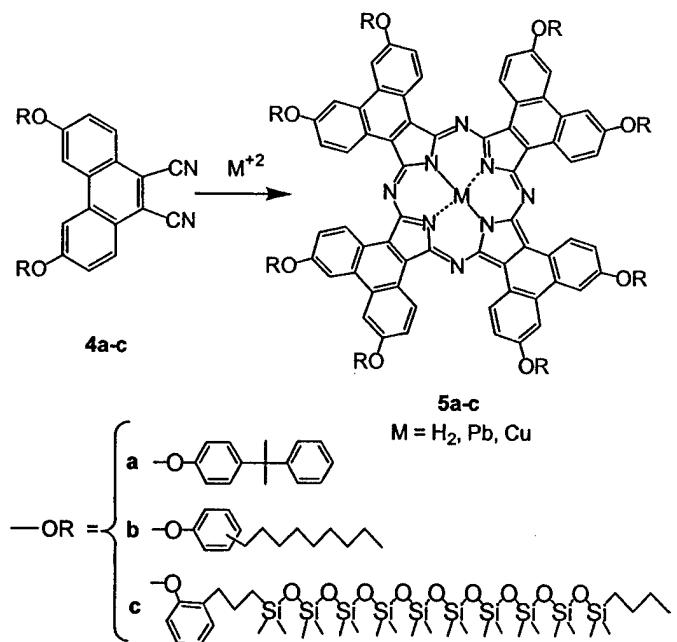
Scheme 3. Synthesis of various substituted phtnanthralocyanines.

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However, the cumylphenoxy group proved insufficient to solublize the phenanthralocyanine moiety. Both the nonylphenoxy and the oligodimethylsiloxane groups did solublize the phenanthralocyanine structure and purification and characterization could be carried out. The oligodimethylsiloxane groups also successfully rendered a liquid character to the corresponding phenanthralocyanine. Nonlinear optical measurements were successfully made on these structures.

IV. Results

a) Phthalocyanine System

The results of physical measurements on this system indicated that the nonoptical physical properties were dominated by the oligodimethylsiloxane structural units. The liquid character of the oligodimethylsiloxane functionalized phthalocyanine compounds and the temperature of its glass transition (-120 °C) are very similar to that for the polydimethylsiloxane linear polymer (-120 °C). When on methyl group is substituted by a phenyl group, the glass transition increases to -46 °C.

For organic dyes in general and phthalocyanine dyes in particular, a tendency to aggregate is very strong. This causes undesired effects on the optical properties which are a broadening of the visible absorption bands and a shortening of the excited state lifetime. The former effect results in a narrowing of the optical transmission window for the limiter material, and the latter effect diminishes the strength of the nonlinear absorption by reducing the amount of reverse saturable absorption. The dimethylsiloxane chain substitution is very effective in depressing the aggregation in solution as well as in

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the neat liquid state. Dimerization is the first step in aggregation of a dye, and the magnitude of the equilibrium constant for this process is a good measure of the aggregating tendency. Typically, dimerization constants range from 10^4 to 10^6 for normal peripherally substituted phthalocyanine compounds. For these oligodimethylsiloxane substituted phthalocyanine compounds, dimerization constants are depressed on the order of two orders in magnitude.

The nonlinear optical properties have two effects that are contributing to the optical limiting: (1) a refractive effect and (2) a reverse saturable absorption effect. The refractive effect is an increasing scattering of light with increasing intensity if irradiation. The change in refractive index with temperature, dn/dT, is a measure of this effect. The polydimethylsiloxane structure has a very large dn/dT (-4×10^{-4} $^\circ$C^{-1}) which is due to the siloxane chain's facile random coil expansion with temperature. With the phthalocyanine chromophore converting light into heat, this mechanism for enhanced optical limiting with these compounds. The measured dn/dT for the phthalocyanine functional analogs is essentially the same as that for the polydimethylsiloxane. The second reverse saturable absorption mechanism is the stronger driver and is very effective in many phthalocyanine optical limiter materials. In the work reported for this program the effects of each mechanism were quantified, and the refractive scattering effect was found to enhance the limiting by 10 to 20% beyond what was obtained by the reverse saturable adsorption effect (see Appendix C).

b) Phenanthralocyanine System

The results of the physical measurements on the phenanthralocyanine system were somewhat unexpected. Despite increasing the number of benzannelated (fused benzene rings) by eight (two for each phthalocyanine benzo ring), the visible adsorption band shifted only marginally to the red and the NMR characterization indicated only a nominal change in ring current of the macroring. These observations and a energy minimization calculation of structure indicated that benzannelation caused a wrapping of the fused ring structure significantly out of planarity. Molecular models displayed a slight steric crowding between the benzannelated rings which also let to the conclusion that the structure was wrapped out of planarity. These results can be viewed in detail in Appendix B.

Optical limiting measurements were made on this phenanthralocyanine ring system, and the results indicated it was a weaker optical limiter than its phthalocyanine analog. It appears the ring wrapping prevented any beneficial effects anticipated from a conjugated delocalization of the benzennelated structure.

V. Summary

The first room temperature intrinsic liquid phthalocyanine compounds were synthesized, characterized and evaluated for an optical limiting application. In addition to a facile processing capability the silicone phthalocyanine materials displayed optical limiting enhancements derived from the oligodimethylsiloxane substituent's diminishing

effect on dye aggregation and from the increased refractive scattering resulting from the large dn/dT of the dimethylsiloxane chain.

The approach aimed at increasing the delocalization by benzannelation to enhance the optical limiting did not realize this objective. The synthesis was fully successful, and characterization indicated that the off-axis benzannelation resulted in a wrapping of the planar structure due to a steric crowding of the benzannelated substituents.

VI. Productivity

a) Publications

1. "Liquid Lead Phthalocyanine Synthesis Development for Optical Limiting Application"
   E.M. Maya, A.W. Snow and J.S. Shirk
   NRL Letter Report Ser 6120-072
   Jun. 6, 2000

2. "Polydimethylsiloxane Substituted Phthalocyanines"
   E.M. Maya, A.W. Snow and J.S. Shirk
   Proceedings of First International Conference on Porphyrins and Phthalocyanines, p. 489 (2000).

3. "Nonlinear Optical Properties of a New Pure Liquid Phthalocyanine"
   S.R. Flom, J.S. Shirk, R.G.S. Pong, A.W. Snow and E.M. Maya
   Polymer Materials Science and Engineering Preprints 83, 224-225 (2000)

4. "Silicon Substituted Phthalocyanines for Optical Limiting Applications"
   E. M. Maya, A. W. Snow, J. S. Shirk, S. R. Flom, R. G. S. Pong, G. L. Roberts
   Polymer Preprints 42(1) 253 (2001).

5. "Peripherally-Substituted Polydimethylsiloxane Phthalocyanines: A Novel Class of Liquid Materials"
   E. M. Maya, James S. Shirk, A.W. Snow, G. L. Roberts
   Chem. Comm. 2001, 615

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6. "Syntheses, Characterization and Properties of Soluble and Liquid Phtnanthralocyanines"
    E. M. Maya, A. W. Snow, J. S. Shirk, S. R. Flom, R. G. S. Pong and J. H. Callahan
    J. Porphyrins and Phthalocyanines <u>6</u>, 463-475 (2002)

7. "Synthesis, Aggregation Behavior and Nonlinear Absorption Properties of Lead Phthalocyanines Substituted with Siloxane Chains"
    E.M. Maya, A.W. Snow, J.S. Shirk, R.G.S. Pong, S.R. Flom and G.L. Roberts
    J. Mater. Chem. <u>13</u>, 1603-1613 (2003)

b) Presentations

1. "Polydimethylsiloxane Substituted Phthalocyanines"
    E.M. Maya, A.W. Snow and J.S. Shirk
    First International Conference on Porphyrins and Phthalocyanines
    Dijon, France
    June 28, 2000

2. "Nonlinear Optical Properties of a New Pure Liquid Phthalocyanine"
    S.R. Flom, J.S. Shirk, R.G.S. Pong, A.W. Snow and E.M. Maya
    ACS National Meeting
    Washington, DC
    August 22, 2000

3. "Polydimethylsiloxane Substituted Phthalocyanines: Synthesis and Characterization"
    E. M. Maya
    George Mason University Seminar
    October 5, 2000

4. "Preparación de Nuevos Derivados de Polidmetilsoloxano con Propiedades Ópticas y Dielectricas Mejoradas"
    E. M. Maya
    Instituto de Ciencia y Technologia de Polímeros, CSIC
    Madrid, Spain
    January 8, 2001

5. "Oligodimethylsiloxane Linked Cyanate Ester Resins"
    E.M. Maya, A.W. Snow, L.J. Buckley
    35th Middle Atlantic Regional Meeting of the American Chemical Society
    George Mason University, Fairfax, VA
    May 28, 2002

VII. Appendices of Publications (a)

"Peripherally-Substituted Polydimethylsiloxane Phthalocyanines: A Novel Class   of Liquid Materials"
E. M. Maya, James S. Shirk, A.W. Snow, G. L. Roberts
Chem. Comm. 2001, 615

Peripherally-substituted polydimethylsiloxane phthalocyanines: a novel class of liquid materials

Eva M. Maya,*[ab] James S. Shirk,[a] Arthur W. Snow[a] and Gerald L. Roberts[b]

[a] Naval Research Laboratory, Washington DC 20375-5342, USA. E-mail: emaya@ccf.nrl.navy.mil
[b] George Mason University, Department of Chemistry, 4400 University Drive, Fairfax, Virginia 22030-4444, USA

Isotropic liquid phthalocyanine compounds with peripheral polydimethylsiloxane oligomer substitution were synthesized and found to have a unique combination of thermo-refractive and nonlinear optical properties along with unusual metal substitution reactivity and aggregation behavior.

Polydimethylsiloxane oligomer substitution at the periphery of a phthalocyanine ring generates a liquid material with exceptional optical properties and chemical behavior. This material is designed to have the rheological and thermorefractive properties of a silicone fluid[1] and the nonlinear optical properties characteristic of the phthalocyanine chromophore.[2] Structure 1 in Scheme 1 combines these molecular features coupled through an aromatic ether linkage. The motivation for this design is to combine two mechanisms important to an optical limiting application[2] into a single compound: a large fluence dependent, refractive index;[1] and a reverse saturable optical absorption.[2] The aromatic ether linkage further incorporates an enhanced photo-oxidative stability. Cloaking of the phthalocyanine ring in a silicone covering has important implications for the chemistries of aggregation and metal substitution. To our knowledge, no examples of peripheral silicone substituted phthalocyanines have been previously reported. In this communication we report synthesis and preliminary characterization of a new class of liquid phthalocyanine (Pcs) materials.

Two routes for the synthesis of the lead and metal-free phthalocyanine compounds are depicted in Scheme 1. Starting reagents for both routes are prepared in the first step. The butyl capped hydrosilyl terminated poly(dimethylsiloxane) (PDMS) oligomer (2) (DP = 9 in this example) is synthesized by an anionic ring opening polymerization of hexamethylcyclotrisiloxane.[3] The allylphenoxyphthalonitrile (3) is prepared by a nitroaromatic displacement reaction of 4-nitrophthalonitrile[4] with 2-allylphenol. In the preferred route, the PDMS oligomer is first coupled to the allylphenoxyphthalonitrile by a hydro-

silylation reaction. Next the allylphenoxyphthalonitrile–PDMS adduct (4) is cyclotetramerized in the presence of lead oxide to yield the phthalocyanine 1a. The alternate route is to first conduct the cyclotetramerization yielding the tetrakis(allylphenoxy)phthalocyanine (5) then to perform the hydrosilylation to yield the phthalocyanine product (1). This route has the disadvantage of a more arduous purification (as a consequence of a required large excess of 2 to ensure a quantitative conversion of the allyl groups) and the use of a heterogeneous non-acidic hydrosilylation catalyst (to avoid displacement of a labile metal from the phthalocyanine cavity).

Structures 1–5 are consistent with spectroscopic characterization.† The phthalocyanine materials have both a mixed isomer and polydisperse character. The phthalocyanine forming reaction produces a statistical mixture of four possible isomers.[5] The polydispersity is a result of the manner in which the butyl capped PDMS oligomer (2) is prepared.[6] These features are regarded as advantages in discouraging liquid crystal formation. In an analogous phthalocyanine system with polyethylene oxide oligomer substituents it was found that a monodisperse system is liquid crystalline[7] while that with a polydisperse system is an isotropic liquid.[8] Liquid crystallinity is detrimental for applications where optical transparency is required.

The PDMS chains determine the liquid character of these materials, which are viscous liquids at room temperatures. The glass transition temperatures, T_g, for the Pb (1a), H₂ (1b) phthalocyanine compounds and the phthalonitrile precursor (4) are 3, 16, and 14 °C respectively. This narrow range of glass transition temperatures is a consequence of the dominant effect of the siloxane chains. A similar trend of a slightly increasing T_g, when progressing from lead to metal-free phthalocyanine with epoxy substituted phthalocyanine glasses, has previously been observed.[9] This trend correlates with a greater tendency of the metal-free phthalocyanine to aggregate relative to the lead phthalocyanine.[10] At rt these phthalocyanine materials will fill short length (~4 μm) optical cells by capillary action over several hours. At elevated temperatures (~100 °C) the viscosity
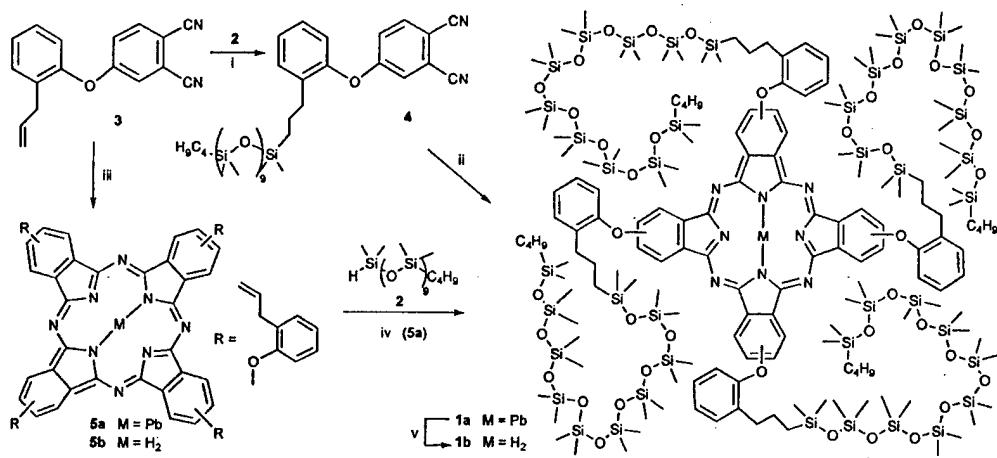
Scheme 1 *Reagents and conditions*: i, 3 drops of 0.1 N solution of H₂PtCl₆6H₂O in isopropanol, 60 °C, 1 h; ii, PbO, 165 °C, 16 h; iii, PbO or hydroquinone, 165–180 °C, 16 h; iv, 8 drops of platinium–divinyl tetramethyldisiloxane complex, toluene, 20 h; v, toluene, F₃CCOOH, 10 min.

is much lower, the aggregation is reduced (spectroscopic detection), and the filling of the cell is much more rapid.

The refractive index of a thin film of the lead phthalocyanine compound (**1a**) was measured by ellipsometry and also by measuring the angle of total internal reflection for a thin film on a prism of known refractive index. Over a temperature range of 24 to 95 °C the refractive index at 1550 nm decreased from

per degree Centigrade and correlates well with the dn/dT reported (4×10^{-4} °C^{-1}) for linear dimethylsiloxane oligomers.[1] This decrease also indicates that the temperature dependence of the refractive index of silicone substituted phthalocyanines is dominated by PDMS chains. Relative to other polymers, polydimethylsiloxane has an exceptionally large dn/dT,[11] and this combination with the phthalocyanine structure demonstrates a successful coupling of this property and this chromophore.

Z-scan and optical limiting measurements were performed on the lead phthalocyanine compound (**1a**) to characterize the nonlinear optical properties. The Z-scan of a 20.2 mM sample of **1a** in a 50.5 μm sample cell at 532 nm is shown in Fig. 1. The material is a strong reverse saturable absorber at 532 nm. An estimate of the excited state cross section from this Z-scan and from a nonlinear transmission experiment on the same sample gave a value of the excited state cross section of ~ 20 times that of the ground state at 532 nm. This implies that the material is a very good reverse saturable absorber. The nonlinear absorbing properties are similar to those found in lead tetrakis(cumylphenoxy)phthalocyanine, PbPc(CP)$_4$.[12] The strong nonlinear absorption, in combination with the large dn/dT reported above, makes this a superior optical limiter material.

Finally, the silicone chains covering the phthalocyanine chromophore impart some unusual chemical behavior, particularly with regard to metal substitution reactions and aggregate formation. When the siloxane–phthalonitrile precursor (**4**) is subjected to the Linstead conditions of lithium pentoxide–pentan-1-ol for conversion to lithium phthalocyanine,[13] a product with a Q-band diagnostic of the dilithium substituted phthalocyanine (675 nm) is obtained. However, it is very difficult to displace the normally very labile lithium with protons. Normally, this occurs under very mild acidic conditions. We find that normal and progressively more severe acid exchange conditions were unsuccessful.‡ Treatment with concentrated HCl and heating resulted in conversion being first observed at 90 °C which became quantitative after 2 h at this temperature. However, once the lithium ion is displaced by the proton, subsequent metal ion substitution reactions proceed under normal conditions.§

The other aspect of unique chemical behavior is in the aggregation tendency. Phthalocyanine compounds aggregate as a concentration dependent association of phthalocyanine rings. The dimerization constant is a useful measure of this aggregation tendency. Typical dimerization constants for phthalocyanine compounds range from 10^4 to 10^6 M^{-1}.[14] Preliminary analysis of concentration dependence of the Q-band absorption using a monomer–dimer equilibrium model indicates that the dimerization constant for **1b** is 150 ± 100 M^{-1}. This is significantly less than the range for phthalocyanine dimeriza-

tion constants mentioned above. We attribute this result to the nature of the siloxane chain and the ortho substitution of the phenylene ether linkage to the phthalocyanine ring.

In summary, the incorporation of PDMS oligomers as phthalocyanine peripheral substituents combines the desirable rheological and refractive properties of a silicone fluid with the nonlinear optical properties associated with the phthalocyanine.

behavior with respect to the phthalocyanine synthesis and aggregation.

Notes and references

† *Selected data* for **1a**; λ(toluene)/nm 721, 648, 365; ν(NaCl)/cm^{-1} 2959 (CH), 1608 and 1492 (C–C), 1253 (SiCH$_3$), 1091 and 1014 (SiOSi), 800 (SiC). For **1b** λ(toluene)/nm 703, 666, 638, 605, 346; ν(NaCl)/cm^{-1} 3295 (NH), 2959 (CH), 1615 and 1479 (C–C), 1259 (SiCH$_3$), 1091 and 1027 (SiOSi), 807 (SiC); *m/z* 4500–2200 consists of peaks separated by 74 amu due to –Si(CH$_3$)$_2$O– degradation which is common to mass spectra of PDMS oligomers.[6] For **2**: δ$_H$(CDCl$_3$, 300 MHz)/ppm 0.04–0.07 (54H, br s, SiCH$_3$), 0.19 (6H, m, SiCH$_3$), 0.53 (2H, m, SiCH$_2$), 0.89 (3H, t, CH$_3$), 1.32 (4H, m, CH$_2$), 4.70 (1H, sept, SiH); ν(NaCl)/cm^{-1} 2972 (CH), 2132 (SiH), 1272 (SiCH$_3$), 1098 and 1027 (SiOSi), 800 (SiC). For **3**: δ$_H$(CDCl$_3$, 300 MHz)/ppm 3.23 (2H, d, CH$_2$), 4.95 (2H, dd, =CH$_2$), 5.78 (1H, m, =CH), 6.95 (1H, d, H$_{arom}$), 7.12–7.33 (5H, m, H$_{arom}$), 7.68 (1H, d, H$_{arom}$); δ$_C$(CDCl$_3$, 75 MHz) 34.0, 108.5, 114.9 and 115.4 (CN), 116.7, 117.6, 120.8, 120.9, 121.0, 126.7, 128.5, 131.6, 132.4, 135.3, 135.4, 151.1, 161.7; ν(NaCl)/cm^{-1} 3082 (=CH$_2$), 2229 (CN), 1615 (C=C), 1595 and 1486 (C–C), 1246; For **4**: δ$_H$(CDCl$_3$, 300 MHz)/ppm 0.012–0.064 (60H, m, SiCH$_3$), 0.51 (4H, m, SiCH$_2$), 0.86 (3H, t, CH$_3$), 1.29 (4H, m, CH$_2$), 1.58 (2H, m, CH$_2$), 2.49 (2H, t, CH$_2$), 6.95 (1H, d, H$_{arom}$), 7.14–7.31 (5H, m, H$_{arom}$), 7.68 (1H, d, H$_{arom}$); ν(NaCl)/cm^{-1} 2966 (CH), 2229 (CN), 1602 and 1492 (C–C), 1254 (SiCH$_3$), 1098 and 1033 (SiOSi), 806 (SiC); For **5a** λ(toluene)/nm 721, 650, 346; ν(NaCl)/cm^{-1} 3076 (=CH$_2$), 2919 (CH), 1638 (C=C), 1608, 1485 (C–C), 1239. For **5b** λ(toluene)/nm 703, 667, 639, 605, 350; ν(NaCl)/cm^{-1} 3295 (NH), 3075 (=CH$_2$), 1638 (CH=CH$_2$), 1611 and 1467(C–C), 1228; δ$_H$(CDCl$_3$, 300 MHz)/ppm −4.1 (s, NH), 3.6 (m, CH$_2$), 5.1 (m, =CH$_2$), 6.1 (m, CH=), 6.8–7.7 (m, H$_{arom}$); *m/z* 1091.

‡ Unsuccessful lithium displacement conditions: aliquot addition of trifluoroacetic acid (10 min); second aliquot addition of trifluoroacetic acid (30 min); aliquot addition of conc. HCl (10 min).

§ Copper and lead ions were substituted into the metal-free phthalocyanine using the acetate salts and refluxing for 2 h in pentan-1-ol–THF.

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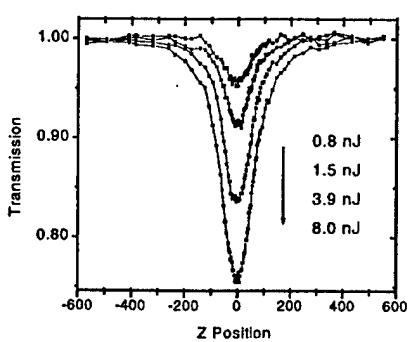
Fig. 1 A Z-scan of a 20.2 mM sample of **1a** at increasing input energy.

VII. Appendices of Publications (b)

"Syntheses, Characterization and Properties of Soluble and Liquid Phtnanthralocyanines"
E. M. Maya, A. W. Snow, J. S. Shirk, S. R. Flom, R. G. S. Pong and J. H. Callahan
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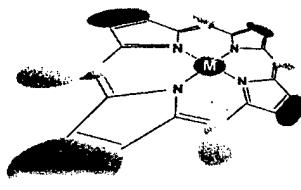
Syntheses, characterization and properties of soluble and liquid phenanthralocyanines

Eva M. Maya*, Arthur W. Snow, James S. Shirk, Steven R. Flom, Richard G. S. Pong and John H. Callahan

Naval Research Laboratory, Washington, DC 20375, USA

ABSTRACT: Phenanthralocyanine compounds with cumylphenoxy, nonylphenoxy and oligodimethylsiloxane phenoxy peripheral substitution were synthesized by nucleophilic aromatic substitution reaction between 3,6-difluoro-9,10-dicyanophenanthrene and the corresponding phenolic precursor. Structural characterization includes IR, NMR, UV-vis and mass spectroscopies. The nonylphenoxy and oligodimethylsiloxane phenoxy phenanthralocyanines were soluble in common organic solvents, and the siloxane product was an isotropic liquid. Compared with the phthalocyanine analog, the Q bands of the Pb, H_2 and Cu phenanthralocyanine were slightly red shifted and variably broadened (small for the Pb compound but large for the H_2 and Cu compounds). The nominal red shift is a consequence of an angular annelation of the benzene rings to the phthalocyanine system. Aggregation was not detected in toluene solution, and the Q band broadening was attributed to a distortion of the tetraazaporphyrin ring to a nonplanar conformation. The siloxane substituted lead phenanthralocyanine neat liquid was evaluated as an optical limiter material. As a neat film a substantial broadening and weakening of the Q band results in a broad visible transmission window and a relatively neutral light olive hue. Upon excitation, there is a rapid decay of the initially excited state so the initial optical limiting is predominately due to a thermorefractive effect rather than a nonlinear absorption. Copyright © 2002 Society of Porphyrins & Phthalocyanines.

KEYWORDS: phenanthralocyanine, optical limiting, cumylphenoxy, nonylphenoxy, dimethylsiloxane, aggregation.

INTRODUCTION

Fusion of benzene rings to the phthalocyanine macrocycle is an approach to extending the plane of conjugation and further developing electrical and optical properties of such materials. Benzannelation of the phthalocyanine chromophore to generate a naphthalocyanine may involve a linear annelation (fusion at the 2,3-position) or an angular annelation (fusion at the 1,2-position) relative to an axis defined by the pyrrole structural units. The syntheses of both of these naphthalocyanine isomers from the naphthalonitrile precursors may be traced back to

Linstead's pioneering work along with the recognition that the 1,2-naphthalocyanine itself consists of four possible geometric isomers [1]. Symmetrical annelation of a second benzene ring to each naphthalo structure generates an anthralocyanine (MAc) from the 2,3-naphthalocyanine and a phenanthralocyanine (MPhc) from the 1,2-naphthalocyanine (Fig. 1). Peripherally unsubstituted anthralocyanine and phenanthralocyanine are both single isomer compounds, and examples of the former [2] and latter [3] were first reported some years ago. Like the phthalocyanine parent, these peripherally unsubstituted benzannelated analogs are generally insoluble to any significant degree in most solvents. However, a most interesting difference in electron

*Correspondence to: Eva M. Maya, email: emaya@ccs.nrl.navy.mil

transport properties was discovered between those analogs with linear versus those with angular benzannelation. Those with linear annelation may display very high electrical conductivity [~] ~~~~~ ~~~~ ~~~~ ~~~~~~ ~~~~~~~~~ ~~~~~~ significantly less electrical conductivity [5-7]. To rationalize the latter case it was suggested that the benzene and tetraazaporphyrin ring systems are not highly conjugated but weakly interact and that the benzo groups exert a shielding effect on the tetraazaporphyrin ring toward electron transfer and transport [5].

Peripheral substitution promotes solubility of these annelated tetraazaporphyrin systems, facilitates study of their optical properties and makes them particularly useful for optical applications that require transparency. One effect of extended conjugation is to shift the Q band from the visible toward the near infrared region of the electronic spectrum. For certain applications, such as optical limiting, this effect is very desirable since the intense color of the phthalocyanine chromophore interferes with visual color discrimination and diminishes perception in the Q band region of the visible spectrum.

The magnitude of the red shift is very dependent on the geometry of the benzannelation. Linear benzannelation causes substantial red shifts to occur in the maxima of the Q band. Shifts of 100 nm per annellated benzene ring are observed in the progression from one (phthalocyanine), two (naphthalocyanine), three (anthralocyanine) to four (tetraaceno-tetraazaporphyrin) benzene ring systems linearly fused to the tetraazaporphyrin ring [8]. When the benzannelation is angular, only small red shifts occur with the addition of one and two fused benzene rings [6, 7].

An elegant molecular orbital calculation and analysis have been performed by Ortí *et al* [9] wherein the origin of the linear and angular annelation effects are found to result from the HOMO being continuously destabilized relative to the LUMO by the addition of fused benzene rings along the pyrrole axis. When the fused benzene rings

are added to the off-axis positions, the HOMO and LUMO are slightly stabilized relative to each other and to the phthalocyanine system with the spectral result of very little shift in the Q band. An additional ~~~~~~ ~~ ~~~~~~~~~~ ~~~~~~~ ~~ ~~~~ ~~~~~~~~ ~~~~~~ calculation is the narrowing of the gap between first and second LUMOs for the MPhc structure. A mechanism for optical limiting by phthalocyanine compounds is a reverse saturable absorption wherein a strongly allowed transition from a long lifetime first excited state to a second excited state occurs on achievement of a threshold first excited state population. The narrowing of the gap between these two excited states appears to have some interesting prospects for shifting the limiting effect to the near infrared and increasing its sensitivity (energy threshold).

To investigate these possibilities the phenanthralocyanine chromophore, preferably with a complexed lead ion, needs to be obtained in a very transparent and concentrated physical form. This has been previously achieved by peripheral substitution with groups that promote high solubility or produce an isotropic liquid state. While naphthalocyanines [10] and anthralocyanines [11] have been made soluble by peripheral substitution, this does not appear to have been done for the phenanthralocyanine. A possible exception is a reported sulfonylation of the unsubstituted parent H_2Phc to promote an unspecified degree of aqueous solubility [12]. For our purposes this is not an attractive option. Phthalocyanines in aqueous systems have very strong tendencies to aggregate [13], and aggregate formation diminishes optical limiting by way of a reduction in excited state lifetime [14]. The complexed lead ion significantly enhances the phthalocyanine chromophore's threshold and response time for optical limiting [15], and this complexed ion is unstable to displacement by protons in aqueous systems. Our approach is to use large neutral organic peripheral groups. In this study the objectives are to synthesize highly soluble and intrinsically liquid lead phenanthralocyanine coupounds, to characterize the structure, chemical and physical properties of this chromophore and to determine its merit as a reverse saturable absorber relative to a comparably substituted lead phthalocyanine compound.

EXPERIMENTAL

All reagents and solvents were of reagent-grade quality, purchased commercially and used without further purification unless otherwise noted. Infrared spectra were obtained from thin film samples using a Nicolet Magna FTIR 750. ^1H, ^{19}F and ^{13}C NMR spectra from solutions were recorded using a Bruker
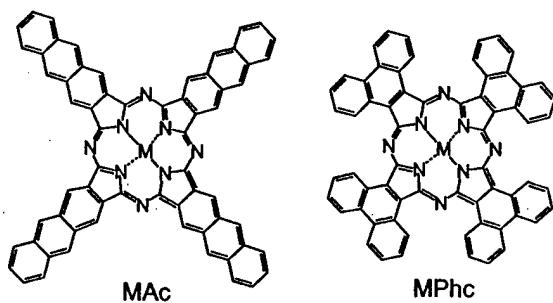

Fig. 1. Structure of anthralocyanine (MAc) and phenanthralocyanine (MPhc)

AC300 NMR spectrometer operating at 300 MHz for ^{1}H, 282 MHz for ^{19}F and 75.5 MHz for ^{13}C with respective chemical shifts internally referenced to tetramethylsilane (0 ppm), CFCl$_3$ (0 ppm) and DMSO-d, acetone-d, or toluene-d. Optical spectra were obtained from solutions and thin films using a Perkin Elmer Lambda 5 UV-vis spectrophotometer. Differential scanning calorimetry (DSC) data were recorded on a DuPont 2100 Thermal Analysis System/910 DSC Module from 3-4 mg samples under a nitrogen atmosphere at 10 °C/sec.

Mass spectrum parent ion measurements were performed using laser desorption time-of-flight mass spectrometry (LD TOFMS). Samples and standards were dissolved in reagent grade methylene chloride at concentrations of 1 mg/ml. Calibration standards were prepared from *meso*-tetraphenylporphyrin (5,10,15,20-tetraphenyl-21H,23H-porphine) (Aldrich) and tetracumylphenoxyphthalocyanine (H$_2$Pc(β-CP)$_4$), a previously characterized phthalocyanine [16]. Both internal and external calibrations were used. For analysis, 1-2 μl of sample was applied to the probe tip and allowed to air dry. If internal calibration was employed, 1-2 μl of calibration solution was subsequently applied to the probe tip. The sample was inserted into the instrument, which is a home-built 1.3 meter flight path linear time-of-flight mass spectrometer. The system was pumped down to 10^{-7} torr and the sample voltage was 20 kV. A nitrogen laser emitting 337 nm light (Laser Sciences, Inc) was used to desorb the sample. The laser beam was focused on the target with a 20 cm lens, and the laser energy (maximum of 200 μj/pulse) was controlled by a beam attenuator. The beam was initially completely attenuated, then the laser power was adjusted until signals were obtained. At threshold, approximately 5-10 μj/pulse was employed to desorb the samples. Spectra were recorded at 1 Hz with digital oscilloscope (LeCroy 9350) and transferred to a PC based data system (TOFWARE) for post-acquisition analysis.

Nonlinear optical measurements. The apparatus for the nonlinear transmission and Z-Scan experiments has been described [17]. The laser source was a doubled Nd/YAG laser with an 8 nanosecond pulse width. The input beam was spatially filtered and then expanded so that only the central 10% entered the focusing optics. This gave the beam an approximately flat top intensity profile. The laser intensity was controlled by wave plate/polarizer combinations.

The light was focused with an f/5 lens to a spot with a measured beam radius of 2.5 ± 0.1 μm at 532 nm. The expected radius for a diffraction limited f/5 beam is 2.2 μm. The light passing through the sample was recollimated and focused onto the detector. An exit aperture was provided at the

recollimating lens. The sample was mounted on a translation stage and translated through the focus for the Z-scan experiments. For nonlinear transmission measurements, the sample was positioned at the focus of the f/5 lens. For nonlinear transmission measurements, the sample position was adjusted about the focus to give the smallest transmitted energy for incident energies near the limiting threshold.

The experiments at low energies were conducted at 10 Hz. For incident fluences above about 10 mJ/cm^2, The repetition rate was reduced to 0.5 Hz. This removed any effect of persistent thermal changes. For incident fluences above about 50 mJ/cm^2, each data point was recorded as a single shot and the sample was translated between the shots to provide a fresh sample for each data point.

Ground state absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

2,3-bis(4-fluorophenyl)-2-butenedinitrile   (2). This procedure is adopted with modification from [18]. Solutions of 40.0 g NaOH in 60 mL distilled water and 0.60 g (3.5 mmol) phenyl trimethylammonium chloride (Aldrich) in 100mL CCl$_4$ were mixed in a 500 mL Erlenmeyer flask, and a solution of 30.0 g (220 mmol) 4-fluorophenyl acetonitrile (Aldrich) in 100 ml CCl$_4$ was slowly added over a 2.5 hr period with very rapid stirring. The mixture develops a red-brown color during the addition. Rapid stirring was continued for 22 hr at room temperature. The precipitated product was collected by filtration and washed twice with 50 mL water. The dark colored precipitate was dispersed in 200 ml CHCl$_3$, filtered, extracted twice with 75 mL 2% HCl, twice with 5% NaHCO$_3$ and dried over anhydrous Na$_2$SO$_4$. Filtration and concentration to dryness yielded 11.7 g (40% yield) of a tan colored product. This crude product was chromatographed on alumina with CHCl$_3$ and recrystallized in several fractions from ethanol to yield a colorless crystalline product. mp 188.5 °C (from [18] 194-195 °C). IR (KBr): v = 3110, 2225, 1600, 1509, 1408, 1255, 1242, 1161, 1097, 864, 840, 783 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.48 (m, 4H), 7.92(m, 4H) ppm. ^{13}C NMR (DMSO-d_6): δ = 116.50 (d), 116.52, 124.56, 128.37, 131.49 (d), 163.62 (d) ppm. ^{19}F NMR (DMSO-d_6): δ = -106.16 (symmetrical 9 line multiplet) ppm.

3,6-difluoro-9,10-dicyanophenanthrene   (3). This procedure is adopted with modification from [18]. A solution of 1.47 g (5.53 mmol) of 2 dissolved in 75 ml CHCl$_3$ and a small crystal of iodine were placed in a 18.5 mm diameter quartz tube reactor fitted with a bubbler inlet tube. The reactor tube was mounted in a Rayonet photochemical reactor fitted with 300 nm lamps and irradiated while bubbling oxygen through the solution at room temperature. The reaction was continued over a 4 day period. Formation of a fine precipitate was observed along

with periodic clogging of the bubbler inlet. At the end of the reaction the product was collected by evaporation of the chloroform and recrystallization from boiling acetone yielding 0.83 g straw colored needles. Yield 56%. mp 291 °C (from [18] 297 °C). IR (KBr): ν = 3095, 2228, 1619, 1523, 1240, 876, 821 cm⁻¹. ¹H NMR (DMSO-d_6): δ = 7.84 (d of d, 2H), 8.21 (d of d, 2H), 8.76 (d of d, 2H) ppm. ¹³C NMR (DMSO-d_6): δ = 110.3 (d), 114.9, 115.0, 119.5 (d), 124.0, 129.8(d), 132.6, 163.4 (d) ppm. ¹⁹F NMR (DMSO-d_6): δ = -104.75 (symmetrical 8 line multiplet with inner 6 lines split into doublets) ppm.

3,6-dicumylphenoxy-9,10-dicyanophenanthrene (4a). To a 35 mL flask fitted with a magnetic stirring bar, Dean-Stark trap, condenser and nitrogen inlet were added 1.01 g (4.77 mmol) of cumylphenol (Aldrich), 0.60 g (2.27 mmol) 3, 6 mL 1-methyl-2-pyrrolidinone and 3 mL of toluene. This mixture was brought to reflux. After 2 hr 0.25 mL water was collected in the trap. The Dean-Stark trap contents were replaced with dry toluene, and the reaction mixture was refluxed overnight under nitrogen. The reaction mixture was concentrated to a ~3 mL volume and added dropwise to 20 mL water to precipitate an olive-brown solid. This suspension was neutralized with HCl and filtered. This solid was dispersed in 30 mL CHCl₃, extracted with 20 mL water, dried over anhydrous Na₂SO₄, passed through an alumina (Woelm, activity 1) column with CHCl₃ elution, concentrated and vacuum dried to yield 0.79 g of a transparent yellow solid which became partially crystalline after 2 days standing. Yield 70%. IR (NaCl): ν = 3089, 3063, 3030, 2969, 2875, 2228, 1620, 1601, 1502, 1441, 1426, 1379, 1364, 1235, 1169, 1020, 763, 700 cm⁻¹. ¹H NMR (DMSO-d_6): δ = 7.03 (s), 7.06 (s), 7.12 (m), 7.25 (m), 7.42 (d of d), 8.02 (d), 8.18 (m), 8.30 (s) ppm. ¹³C NMR (DMSO-d_6): δ = 26.4, 38.1, 107.6, 109.5, 111.0, 115.0, 116.8, 118.8, 121.6, 122.4, 124.0, 124.4, 124.9, 127.8, 142.6, 146.1, 149.0, 155.1 ppm.

3,6-dinonylphenoxy-9,10-dicyanophenanthrene (4b). To a 35 mL flask fitted with a magnetic stirring bar, Dean-Stark trap, condenser and nitrogen inlet, were added 1.05 g (4.77 mmol) of nonylphenol (Aldrich, purified by column chromatograpy on silica gel with toluene elution), 0.600 g (2.27 mmol) of 3,6-difluoro-9,10-dicyanophenanthrene 3, 0.66 g (4.77 mmol) of potassium carbonate, 6 mL of 1-methyl-2-pyrrolidinone and 3 mL of toluene. This mixture was refluxed overnight under nitrogen. Wet toluene collected in the Dean-Stark replaced by dry toluene after a few hours. The mixture was concentrated at reduced pressure (10 mm Hg, 120 °C) to yield a brown oil. This crude product was dissolved in 20 mL of CH₂Cl₂, washed three times with 20 mL of 1% HCl and three times with 20 mL of distilled water. The CH₂Cl₂ phase was separated and dried over anhydrous

MgSO₄. After filtration and solvent evaporation, the TLC analysis of the oil obtained showed the starting materials as impurity. The compound was then purified by column chromatography on silica with toluene elution. Yield 0.979 g (65%). IR (NaCl): ν = 2950, 2229, 1621, 1500, 1233, 1010 cm⁻¹. ¹H NMR (acetone-d_6): δ = 0.64-1.55 (2xm, 38H), 7.15 (s, 4H), 7.49 (m, 6H), 8.05 and 8.19 (m, d, 4H) ppm.

3,6-di(butyloligo(dimethylsiloxy)trimethy-lenephenoxy)-9,10-dicyanophenanthrene (4c). Synthesis of reagent: butyloligo(dimethylsiloxy)tri-methylenephenol. To a 25 mL flask were added 0.350 g (2.61 mmol) of 2-allylphenol (Aldrich) and 3 drops of a 0.1N solution of hydrogen hexachloroplatinate(IV) hydrate (H₂PtCl₆) in 2-propanol. The mixture was heated at 60 °C and 2.04 g (2.61 mmol) of butyl capped hydrosilyl terminated polysiloxane oligomer (HSi(CH₃)₂[OSi(CH₃)₂]₉C₄H₉) [19] were added. The mixture was stirred for a hour. The light brown oil obtained was purified by column chromatography on silica with toluene elution to give colorless oil. Yield: 1.94 g (81%). IR (NaCl): ν = 3476, 2966, 1459, 1266, 1098, 1033 and 813 cm⁻¹. ¹H NMR (acetone-d_6): δ = 0.08-0.10 (m, 60H), 0.60 (m, 4H), 0.87 (t, 3H), 1.34 (m, 4H), 1.60 (m, 2H), 2.52 (m, 2H), 6.74-7.08 (m, 4H), 8.22 (s, 1H) ppm. ¹³C NMR (acetone-d_6): δ = 0.38, 1.40, 14.08, 18.51, 18.88, 24.41, 26.14, 27.00, 34.60, 115.67, 120.05, 127.47, 129.50, 130.84, 155.93 ppm.

To a 35 mL flask fitted with a magnetic stirring bar, Dean-Stark trap, condenser and nitrogen inlet, were placed 1.73 g (1.88 mmol) of butyloligo(dimethyl-siloxy)trimethylenephenol, 0.250 g (0.94 mmol) of 3,6-difluoro-9,10-dicyanophenanthrene 3, 0.259 g (1.88 mmol) of potassium carbonate, 2.5 mL of 1-methyl-2-pyrrolidinone and 1.25 mL of toluene. This mixture was refluxed overnight under nitrogen. Wet toluene collected in the Dean-Stark replaced by dry toluene after a few hours. The mixture was concentrated at reduced pressure (10 mm Hg, 120 °C) to yield a brown oil. This crude product was dissolved in 20 mL of CH₂Cl₂, washed three times with 20 mL of 1% HCl and three times with 20 mL of distilled water. The CH₂Cl₂ phase was separated and dried over anhydrous MgSO₄. After filtration and solvent evaporation, the TLC analysis of the oil obtained showed the starting materials as impurity. The compound was then purified by column chromatography on silica with toluene elution. Yield: 0.54 g (28%). IR (NaCl) ν = 2950, 2229, 1628, 1266, 1111, 1026, 820, 703 cm⁻¹. ¹H NMR (acetone-d_6): δ = -0.07-0.18 (m, 120H), 0.56 (m, 8H), 0.99 (t, 6H), 1.34 (m, 8H), 1.62 (m, 4H), 2.62 (m, 4H), 7.15 (m, 2H), 7.32 (m, 4H), 7.42 (m, 2H), 7.60 (m, 2H), 7.82 (s, 2H), 8.33 (d, 2H) ppm.

Octa(cumylphenoxy)phenanthralocyanine, M = H₂ (5a). A mixture of 3 mL dry toluene

(freshly distilled, center cut) and 15 mL 1-pentanol (previously stored over 4 Å molecular sieves) was distilled under nitrogen. The toluene and first 5 mL 1-pentanol were discarded, and the second 5 mL

reaction flask. This flask was fitted with a stirring bar, thermometer, condenser and nitrogen inlet and 3 mL dry toluene and 0.0053 g (0.23 mmol) of 30% lithium/mineral oil dispersion (Johnson Matthey) were added. This mixture was refluxed for 1 hr, cooled to 50 °C, and 0.24 g (0.37 mmol) **4a** dissolved in 3 mL dry toluene added. This mixture was refluxed under nitrogen for 18 hr with gradual development of an intense green-blue observed. This mixture was added dropwise to 30 mL of rapidly stirred acetic acid. After 1 hr the precipitated crude product was collected by centrifugation, washed twice by suspending in methanol and centrifuging, washed with ether and vacuum dried to yield 0.10 g of a purple solid. This product was insoluble in $CHCl_3$, toluene and chloronaphthalene. Attempted dissolution in 1-methyl-2-pyrrolidinone resulted in a faint blue-green solution with a very weak Q band absorption at 700 nm similar to that observed for the unsubstituted analog [5]. Yield 42%. IR (NaCl): ν = 3300 (N-H), 3084, 3057, 3030, 2966, 2928, 2867, 1617, 1602, 1584, 1502, 1443, 1418, 1235 (C-O), 1181, 1168, 1014, 978, 762, 699 cm^{-1} (see Fig. 2). MS: m/z 2596 (2595 calc).

Octa(nonylphenoxy)phenanthralocyanine, M = Pb (5b). To a 10 × 75 mm tube were added 0.500 g (0.75 mmol) of 3,6-dinonylphenoxy-9,10-dicyanophenanthrene (**4b**), 0.129 g (0.58 mmol) of PbO (Fisher) and an stirring bar. This mixture was degassed (~1 torr) with gentle warming until bubbles ceased (5 min) and sealed under vacuum. The tube was heated at 230 °C with stirring for two days. The crude product was dissolved in 10 mL of CH_2Cl_2, filtered and concentrated. The product was purified by passing through a silica column (Fluka AG 60, activity 2-3) with toluene elution. First fractions were contaminated with a tricyano triazine impurity [20]. The subsequent pure fractions yielded a green solid after concentrating and vacuum drying (2 h at 80 °C). Yield: 0.207 g (40%). IR (NaCl): ν = 2959, 1614, 1511, 1421, 1240, 990 cm^{-1}; UV (toluene): λ = 731, 660, 448 nm (see Fig. 5).

Octa(nonylphenoxy)phenanthralocyanine, M = H_2 (5b). 0.200 g (0.072 mmol) of octa-(nonylphenoxy) lead Phc were dissolved in 10 mL of CH_2Cl_2 and a couple of drops of trifluoro acetic acid were added. The mixture was stirred 10 min at room temperature. The solution was concentrated and passed through an alumina column with CH_2Cl_2 elution. Yield: 0.128 mg (67%). IR (NaCl): ν = 3302, 2966, 1621, 1511, 1421, 1240, 990 cm^{-1} (see Fig. 2). UV (see Fig. 5). ^{1}H NMR (see Fig. 4). MS (see Fig. 3).

Octa(nonylphenoxy)phenanthralocyanine, M = Cu (5b). 0.100 g (0.037 mmol) of octa-(nonylphenoxy) metal free Phc and 0.37 g (1.85 mmol) of copper acetate were heated at reflux 3 mL of THF under nitrogen atmosphere for 4 hours. After concentrating, the product was extracted with CH_2Cl_2, washed three times with water, dried over anhydrous $MgSO_4$, filtered and concentrated to dryness. The compound was then purified by column chromatography in silica with toluene elution. Yield 0.019 g (19%). This compound can also be prepared following the same procedure described for M = Pb. In this case, copper bronze was used instead of lead oxide and the temperature reaction was increased to 270 °C. IR (NaCl): ν = 2966, 1629, 1589, 1511, 1421, 1240, 990 cm^{-1}. UV (toluene): λ = 669, 646, 497 nm (see Fig. 5).

Octa(butyloligo(dimethylsiloxy)trimethylene-phenoxy)phenanthralocyanine, M = Pb (5c). To a 10 × 75 mm tube were added 0.500 g (0.24 mmol) of 3,6-di(butyloligo(dimethylsiloxy)trimethylenephe-noxy)-9,10-dicyanophenanthrene (**4c**), 0.041 g (0.184 mmol) of PbO (Fisher) and an stirring bar. This mixture was degassed (~1 torr) with gentle warming until bubbles ceased (5 min) and sealed under vacuum. The reaction mixture was heated two days at 230 °C with stirring. The crude product was dissolved in 10 mL of toluene, filtered and concentrated to dryness. The product was purified by passing through a silica column (Fluka AG 60, activity 2-3) with toluene elution. First fractions were contaminated with a tricyano triazine impurity [20]. The pure fractions were evaporated and the green liquid obtained was vacuum dried for 2 h at 80 °C. Yield: 0.167 g (32%). Tg = -125 °C. IR (NaCl): ν = 2971, 1497, 1415, 1265, 1108, 1026, 807 cm^{-1}. UV (toluene): λ = 730, 652, 448 nm.

RESULTS AND DISCUSSION

Synthesis and peripheral group design

The synthesis of the dicyanophenanthrene precursors to the phenanthralocyanine is depicted in Scheme 1. Synthesis of 3,6-difluoro-9,10-dicyanophenanthrene (**3**) from 4-fluorobenzylcyanide (**1**) through photochemical cyclodehydrogenation of the α,α'-dicyano-trans-stilbene intermediate (**2**) follows the route reported for the unsubstituted 9,10-dicyanophenanthrene [21] and later reported for **3** in a patent [18]. In the third step solublizing peripheral groups are bonded to the dicyanophenanthrene by a nucleophilic aromatic displacement reaction by a substituted phenol for the fluorine to yield the desired aryloxy substituted dicyanophenanthrene (**4a-c**).

The yields of these three products indicate that the two cyano groups are sufficient to activate the fluorine for this displacement reaction in the phenanthrene aromatic structure.

The cumylphenoxy group was initially selected as the peripheral substituent to solublize the phenantralocyanine structure. Previous work with the phthalocyanine substituted analog indicated that solubility in toluene is as high as 10% by weight and that conversion of the phthalonitrile analog to the phthalocyanine may be accomplished with a weak reducing agent like hydroquinone [22]. However, the cumylphenoxy substituted dicyanophenanthrene (**4a**) is less reactive toward tetraazaporphyrin formation as observed previously with the unsubstituted analog [5], and Lindstead's lithium amylalkoxide conditions were initially used [23]. This reaction (Scheme 2) yielded a crude product (**5a**, M = Li) which is worked up under acidic conditions to displace the lithium ions by protons. This product is insoluble in most organic solvents and could not be further purified by chromatography or sublimation.

The infrared spectrum of the product purified by exhaustive extraction (see Fig. 2) was very similar to that of the precursor **4a** except that the nitrile band has been replaced by the N-H stretching band (3300 cm^{-1}) characteristic of the metal-free tetraazaporphyrin and previously observed for the unsubstituted H$_2$Phc analog [5]. A trace solubility in N-methyl pyrrolidone made possible the observation of a broad Q band at 700 nm. The very poor solubility of **5a** is unexpected with respect to behavior for the phthalocyanine system. An alternate and direct synthesis to lead phthalocyanine uses lead oxide as the co-reactant [24] and has proven successful with less reactive silicone substituted phthalocyanines [19]. However, this lead oxide route with **4a** yielded a product with insolubility similar to metal-free **5a**. Conjecture for this solubility difference with the cumylphenoxy substituted phthalocyanine was that the phenanthralocyanine might have a much stronger tendency to aggregate or that its non-mixed isomer structure might promote a solvent resistant crystal structure. Use of more strongly solubilizing peripheral groups indicates both of these conjectures to be incorrect.

The nonylphenoxy and the dimethylsiloxy oligomer peripheral groups were selected as substituents that would promote higher solubility and in the latter
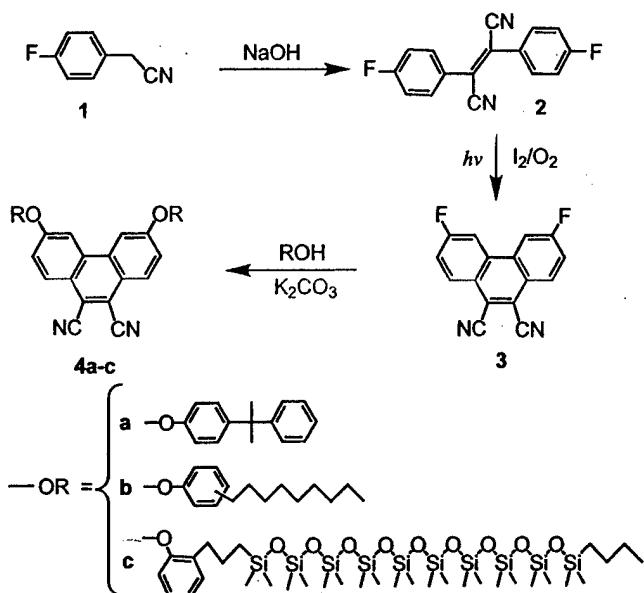
Scheme 1. Synthesis of 3,6-disubstituted 9,10-dicyanophenanthrenes (**4a-c**)
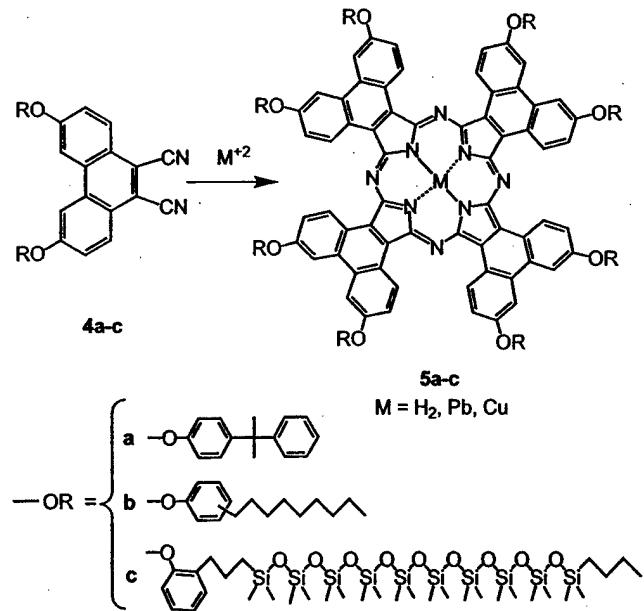
Scheme 2. Conversion of the 3,6-disubstituted 9,10-dicyanophenanthrene to the phenanthralocyanine (**5a-c**)

case isotropic liquidity. Previous work has indicated this to be the case when the dimethylsiloxy oligomer group is used with the phthalocyanine system [19]. Of further particular interest in that work was the silicone's thermorefractive enhancement of the optical limiting associated with the phthalocyanine chromophore [19]. While this silicone oligomer substituent is very effective for these purposes, it has a dispersity of chain length [25] and an instability under mass spectrum acquisition conditions [26] that make it somewhat difficult to obtain quantitative measurements. The nonylphenoxy group was

selected to circumvent these difficulties for obtaining the necessary structural characterization and optical properties of the phenanthralocyanine Q band in solution.

Both **4b** and **4c** were converted using the lead oxide coreactant to the corresponding lead phenanthralocyanine, **5b** and **5c** according to Scheme 2. The lower reactivity of the dicyanophenanthrene relative to phthalonitrile necessitated higher reaction temperatures (230 vs 160 °C) and longer reaction times (24-48 hr vs 12 hr) for this conversion. A trace of triazine byproduct was observed (detected by weak bands of 2221, 1640 and 1520 cm^{-1}) [20] and separated by column chromatography. These compounds are soluble in solvents such as chloroform and toluene, and **5c** is an isotropic liquid at room temperature. Both **5a** and **5b** may be converted to the metal-free analog by reaction with trifluoroacetic acid. The silicone oligomer substituent of **5c** appears to retard the proton displacement of the lead ion, and only partial conversions to the metal-free analog were achieved. A similar effect where the oligomeric silicon substiturent retarded displacement of lithium ion by protron in an analogous phthalocyanine system has been observed [19].

Characterization

The infrared spectra of the metal-free analogs of **5a-b** are depicted in Fig. 2. The informative bands are the N-H stretching mode at 3300 cm^{-1} characteristic of the cavity protons bonded to the pyrrole nitrogen atoms, the C-O stretching mode at 1240 cm^{-1} corresponding to the peripheral group's ether linkage and the C-H bending modes at 720 and 760 cm^{-1} characteristic of the phenanthrene structure [3, 5].

The mass spectra of **5a** and **5b** (M = H$_2$) were obtained by LD TOFMS. The spectrum of **5a** exhibited a single parent ion at 2596.8 in good agreement with an average MW of 2597.2. The spectrum of **5b** is presented in Fig. 3. This spectrum contains parent ions of the two internal calibrants, *meso*-tetraphenylporphyrin (nominal MW 614, average MW 614.8) and tetracumylphenoxyphthalo cyanine (nominal MW 1354, average MW 1355.7), along with a molecular ion cluster for **5b**. For **5b** two closely spaced parent ions were observed at m/z = 2662 and m/z = 2676. The lower number is in good agreement with the calculated average mass of 2661.7, and the higher number probably correlates with addition of a heteroatom. Adsorption of oxygen atoms has previously been observed in the mass spectra of the phenanthralocyanine structure [16]. However, the resolution of this measurement is insufficient to establish whether the higher mass peak (a mass difference of 14 mass units from the molecular ion) results from a combination of hydrogen loss
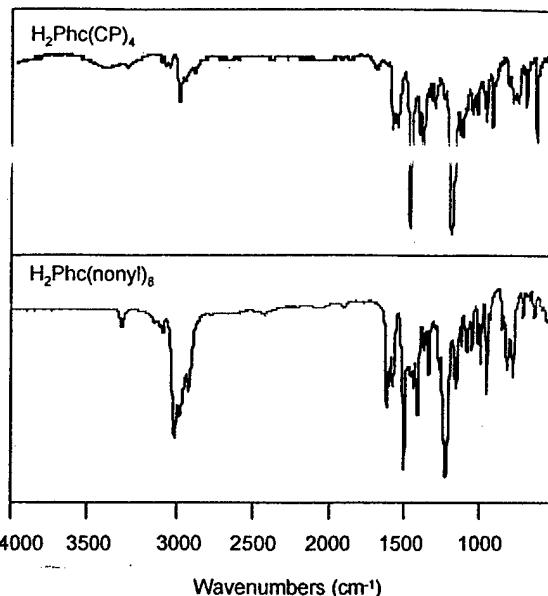
Fig. 2. Infrared spectra of (a) the cumylphenoxy substituted metal-free phenanthralocyanine **5a** and (b) the nonylphenoxy substituted metal-free phenanthralocyanine **5b**

and oxygen addition, or some similar process with a different heteroatom (e.g. N). A second major feature in the molecular ion cluster is a broad peak centered 80 mass units below the molecular ion. This peak results from a fast unimolecular decomposition of the molecular ion, based on the broadness of the feature and the absence of correlation with a distinct mass fragment (e.g. the nonyl group or phenylnonane group). Attempts to obtain a mass spectrum of **5c** (M = H$_2$) were unsuccessful. Attempts to detect the parent ion in the mass spectrum of a dimethylsiloxy oligomer functionalized phthalocyanine analogue have also been unsuccessful and attributed to -Si(CH$_3$)$_2$O- chain degradation commonly observed with silicone oligomers [19].

The ^{1}H NMR of **5b** (M = H$_2$) is presented in Fig. 4. There are five broad but resolved aromatic proton resonances. The three resonances at 10.2, 10.0 and 9.8 ppm correlate with those of the phenanthrene structure at the respective 4, 1 and 2 positions and are downfield shifted by the tetraazaporphyrin ring current. The two resonances at 8.0 and 7.75 correlate with the phenylene resonances of the nonylphenoxy peripheral groups. The N-H resonance is detected as a weak broad signal at -1.6 ppm. This upfield chemical shift is a consequence of the tetraazaporphyrin ring current. This shift is frequently amplified to positions as high as -8 to -9 ppm [20] by aggregation effects from the cofacial association of tetraazaporphyrin rings. Aggregation is a dynamic equilibrium process, and its effects may be diagnosed by concentration and particularly by temperature effects [27]. The N-H resonance in the spectrum of **5b** remained
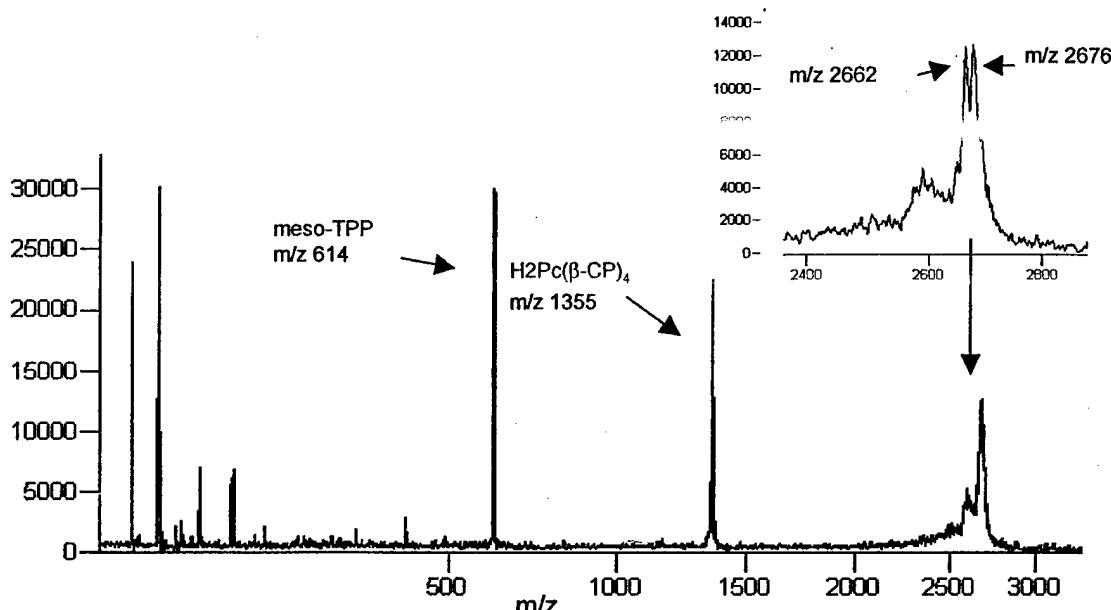
Fig. 3. Mass spectrum of the nonylphenoxy substituted metal-free phenanthralocyanine. The metal-free tetraphenylporphyrin (TPP) and tetracumylphenoxy phthalocyanine $H_2Pc(\beta-CP)_4$ reference compounds were used for calibration

constant (-1.62 ± 0.02 ppm) as the temperature was varied from 23 to 50 °C. The relatively small upfield chemical shift of this resonance and its insensitivity to temperature are consistent with a tetraazaporphyrin having little tendency to aggregate.

The electronic spectra of **5b** (M = Pb, H_2, Cu) in dilute toluene solution are displayed in Fig. 5. Compared with the phthalocyanine system, the Q band band of this PbPhc complex is broader and only slightly red shifted (approximately 10 nm). The extinction coefficient at the Q band wavelength maximum (731 nm) is 110,000 $M^{-1}.cm^{-1}$ which is about half that of the phthalocyanine analog. This diminishment 'in intensity may be attributable to the spectral broadening or possibly related to an electronic perturbation by the fused benzene rings. The B band at 450 nm is substantially red shifted (approximately 100 nm) from the phthalocyanine system. This large red shift of the B band is predicted by Ortí's calculation [9]. The electronic spectrum of **5c** (M = Pb) in toluene solution (not shown) is indistinguishable from that of **5b** (M = Pb).

Displacement of the lead ion by protons yields **5b** (M = H_2) which displays a Q band with a much greater degree of broadening (Fig. 5b) than might be anticipated from analogy with the **5b** (M = Pb) or with the phthalocyanine system. The symmetry change from D_{4h} to D_{2h} (if planarity is presumed) is well known to cause a splitting and some broadening of the Q band. However, the broadening and spectral shape appear to indicate that additional effects are occurring. The broad maximum in the Q band at 640 nm has the appearance of what would be expected for an aggregating system. Contrary to this, the Q band shape does not vary with concentration even
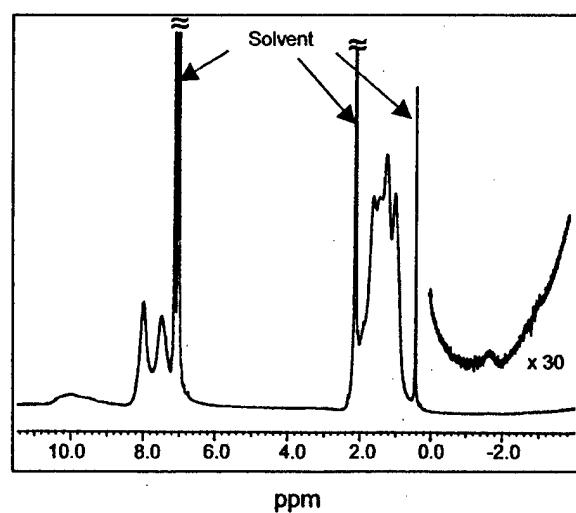
Fig. 4. ^1H NMR spectrum of the 0.005 M nonylphenoxy substituted metal-free phenanthralocyanine **5b** in toluene solution

at high dilution. If aggregation at low to moderate concentrations (10^{-7} to 10^{-3} M) were occurring, a concentration dependence would be expected. The observation of the cavity protons' resonance in the ^1H NMR spectrum having very little if any temperature dependence (described above) is also not consistent with a strong tendency to aggregate.

To further probe the electronic spectrum's dependence on cavity substitution as well as the chemical substitution behavior of this MPhc system, **5b** (M = Cu) was prepared. Initially, this complex was prepared from the metal-free analog by exchange reaction with copper acetate. The electronic spectrum displayed a very broad Q band
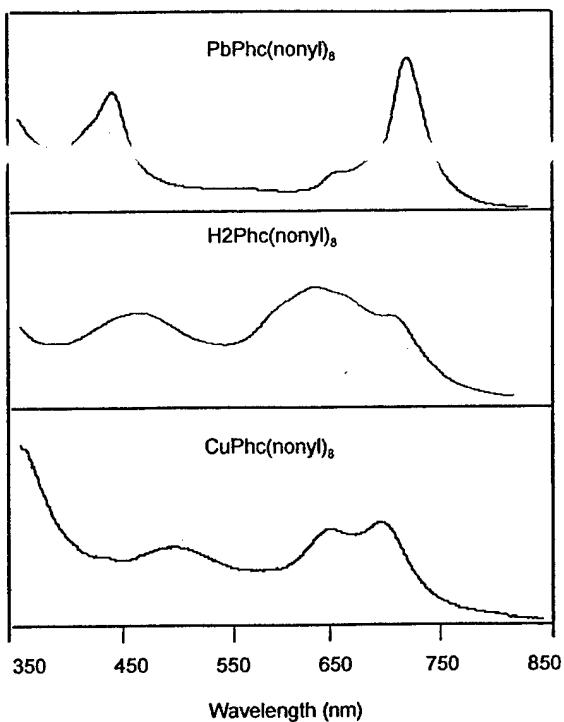
Fig. 5. Electronic spectra of the nonylphenoxy substituted phenanthralocyanine **5b** with M = Pb, H$_2$, Cu in ~10^{-4} M toluene solution

with a curious shape (Fig. 5c). To confirm that this spectrum is representative of **5b** (M = Cu), an alternate preparation was conducted where the dicyanophenanthrene (**4b**) is reacted directly with copper bronze in a mode similar to that reported for copper phthalocyanine formation [28]. The spectrum of the product from this reaction was identical to that from the exchange reaction.

We associate the broadened characteristics of the spectra in Fig. 5 with a distortion of the structure of the MPhc chromophore from planarity. The distortion results from steric crowding of substituent groups bonded at the phthalocyanine α-positions (1,4,8,11,15,18,22,25-positions). X-ray crystal structure studies have shown that substitution at all of these α-positions with alkyl [29] and alkoxy [30] groups causes the phthalocyanine ring to distort to a saddle shaped conformation. The steric crowding requires that substituents at two adjacent α-positions force the ring distortion and consequent Q band broadening. In the visible spectrum, the α-substitution effect on Q band broadening has been observed by systematic substitution of methyl-terminated oxyethylene at four β-positions, four α-positions and eight α-positions [31]. Progressing from the tetra-β-substituted isomer to the tetra-α-substituted isomer (in this case the 1,8,15,22-α-isomer is predominant from synthesis considerations [32, 33]) a very small amount of broadening occurs as the pocket between adjacent α-positions can accommodate one

substituent. For the case of the octa-α-substituted phthalocyanine, forcing two α-substituents into this pocket may cause significant distortion and spectral broadening depending on the substituent ~~size or conformational constraints. Substitu~~ the α-positions also has a remarkably strong effect in diminishing the phthalocyanine tendency to aggregate [34, 35], and, consistent with the lack of a Q band spectrum dependence on concentration, aggregation is not believed to be a contributor to the broadening of the spectra in Fig. 5.

While we are not able to quantify distortion of the MPhc structure from planarity with a crystal structure, an energy minimization calculation on the metal-free compound was carried out using the MM2 routines provided in Chem 3D. Two energy minimized structures corresponding to saddle and propeller conformations are shown in Fig. 6. Both conformations in this figure clearly demonstrate the crowded spatial overlap of the hydrogen atoms bonded to the benzannelated α-carbon positions (i.e. the 1 and 8 positions of the phenanthrene precursor structure). In addition there is apparent overlap of these hydrogens with the lone pairs of the aza ring nitrogen. This steric crowding must be relieved through warping of the ring system. Other distorted conformations also appear to be of appreciable stability, and this may amplify the amount of spectral broadening observed. It may be that metal ions with particular coordinating characteristics might preferentially stabilize one of the warped ring conformations. For instance, the propeller conformation shown is Fig. 6b may be relevant to metal-substituted complexes such as lead where the metal ion is too large to fit in the plane of the cavity.

Nonlinear optical properties

One motivation for the synthesis of the phenanthralocyanine **5c** (M = Pb) was the potential for optical limiting applications. The chromophore is related to the Pb phthalocyanines that are very efficient nonlinear absorbers and the isotropic liquid character of the pure material enables the preparation of nonscattering thin films of high optical quality. Here we evaluate the potential of a pure lead phenanthralocyanine film for optical limiting applications. Detailed studies of the nonlinear optical properties will be published separately.

The optical experiments were performed on a thin film of the lead phenanthralocyanine, **5c**, in a cell with a path length of 4.09 μm. The glass transition of **5c** is -125 °C as measured by DSC, and this liquid exhibits no birefringence when observed by optical microscope under crossed polarizers. The liquid character of **5c** made it possible to fill this short path length cell by capillary action.

a)   (b)
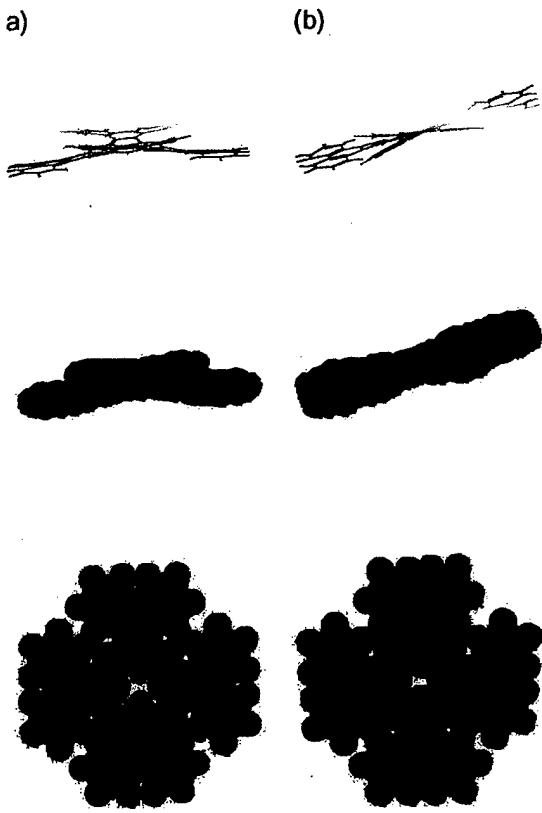
Fig. 6. a) Saddle Conformation of H₂Phc. b) Propeller Conformation of H₂Phc

The visible spectrum of the lead phenanthralocyanine film is shown in Fig. 7a. The relatively flat absorption in the phenanthralocyanine film is notable. The transmission of the film is greater than 70% over the range between 500 nm and 665 nm. The film is a light olive color to the eye. Figure 7b displays a spectrum of the siloxane substituted phthalocyanine analog [19] in a 4.22 μm cell for comparison. The transmission window in the visible spectrum of the Pb phenanthralocyanine film is substantially broader than the Pb phthalocyanine analog. It is also much broader than another analogous phthalocyanine limiter material, lead tetrakis-cumylphenoxy phthalocyanine in solution [15]. The latter is one of the phthalocyanines known to be most useful for optical limiting.

The transmission window of the phenanthralocyanine is broader and flatter than the corresponding phthalocyanines primarily because the Q band is relatively weak in the phenanthralocyanine film. This, of course, is partly because the molecular volume per chromophore is larger in the phenanthralocyanine, but even when normalized for the concentration, the absorption coefficient of the phenanthralocyanine Q band in the pure thin film is more than an order of magnitude smaller. In the transmission window (500-600 nm), the absorption coefficient of the dimethylsiloxy phthalocyanine and

phenanthralocyanine are similar to each other, and both are larger than that of the tetrakis-cumylphenoxy phthalocyanine [15].

The transmission as a function of incident fluence at 532 nm of the pure liquid phenanthralocyanine film is shown in Fig. 8. This experiment measures the contribution of nonlinear absorption (reverse saturable absorption) to an optical limiter based on this material. These data were taken with a pulse width of 5 nanoseconds in an optical system with approximately f/5 optics. There are two distinct regions in the nonlinear transmission. There is a weak nonlinear absorption for fluences up to about 100 mJ/cm² and then a much stronger nonlinear absorption at fluences above 100 mJ/cm². The initial nonlinear absorption is just discernable in Fig. 8. It was verified by careful Z-scan studies at these fluences.

The nonlinear absorption of a thin film of phenanthralocyanine 5c is weak, but there is also a nonlinear refractive contribution to an optical limiter. The nonlinear refractive contribution on a nanosecond time scale was evaluated using a Z-scan
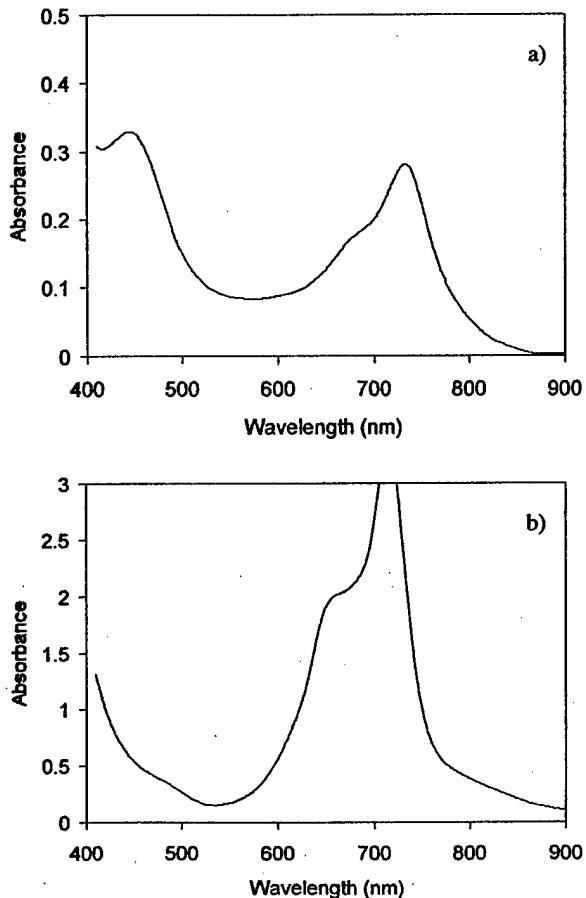
Fig. 7. The electronic spectrum of: a) Pure liquid lead phenanthralocyanine (5c) in a cell with a path length of 4.09 μm. b) Pure liquid lead phthalocyanine analog (lead phthalocyanine with peripheral oligodimethylsiloxane substituents [19]) in a cell with a path length of 4.22 μm
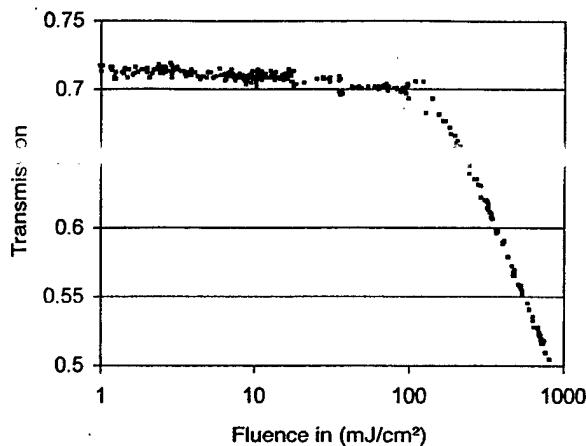
Fig. 8. The transmission as a function of incident fluence at 532 nm for a 4.09 μm sample of pure liquid PbPhc


Fig. 9. The refractive contribution to the Z-Scan of pure liquid phenanthralocyanine, **5c**, at 532 nm. The input fluences for the two curves are 5.5, and 30 mJ/cm²

technique [36]. The open aperture Z-scan showed a small but clear nonlinear absorption consistent with the nonlinear transmission experiment. The closed aperture Z-scan is shown in Fig. 9. This figure shows the transmission as the sample is translated through the focus of a laser with a 40% transmission aperture at the output lens. The transmission is normalized by the open aperture transmission. Qualitatively, Figure 9 shows that the phenanthralocyanine film exhibits a strong nonlinear refraction with a negative sign; i.e. the refractive index decreases with fluence. We estimate the relative contributions of refraction and absorption to an optical limiter by comparing the relative transmission at the minimum of the Z-scans in Fig. 9 with the relative change in transmission at the same fluence in Fig. 8. The nonlinear refraction contribution to an optical limiter will dominate the nonlinear absorption at fluences below 100 mJ/cm².

The origin of the nonlinear optical properties of this class of molecules can usually be traced to the excited state dynamics. Some of the pertinent processes are illustrated in Fig. 10. A strong nonlinear absorption requires that both the excited state cross-section σ_{ex} is much greater than the ground state cross-section σ_0, and the relaxation times τ_1 and τ_{ex} are long. In the phenanthralocyanine film, the initial response included a weak nonlinear absorption and a strong nonlinear refraction. Such a result is expected if the excited state lifetime, τ_1, is short and much faster than τ_2. In this case the quantum yield for formation of the absorbing excited state is small, and nonlinear absorption in a nanosecond experiment is also small. The high quantum yield for internal conversion leads to the rapid conversion of most of the absorbed energy to heat and to a thermally induced change in the index of refraction. This is consistent with the observed large nonlinear refraction. The magnitude of the nonlinear refraction also reflects the excellent thermorefractive properties of this material.

We also observed a very strong nonlinear
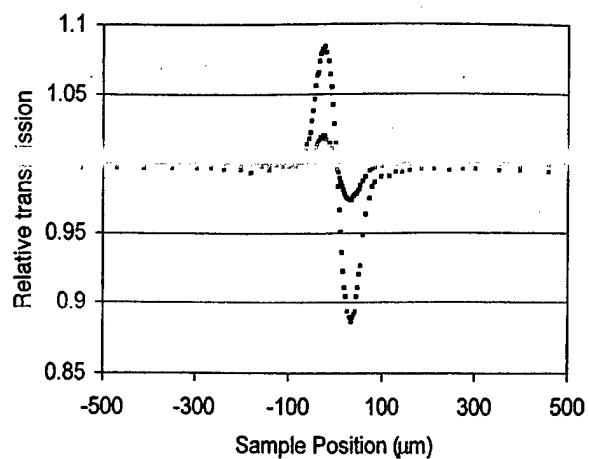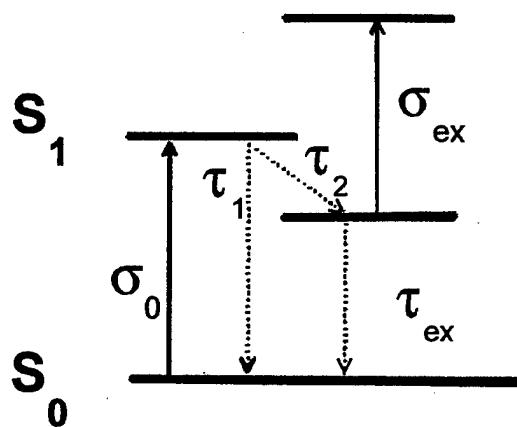
Fig. 10. Low lying energy levels in a nonlinear absorber such as the phenanthralocyanine **5c** (M = Pb). The ground state absorption coefficient is σ_0, the excited state absorption coefficient is σ_{ex}. τ_1 is the relaxation time to the ground state, τ_2 is the relaxation time to the absorbing excited state and τ_{ex} is the relaxation time of the absorbing excited state to the ground state

absorption at fluences greater than 100 mJ/cm². This fluence dependence of this absorption is consistent with a higher order nonlinearity. It is probably due to multiphoton processes. Further work is necessary to determine the mechanism, but it is clear from Fig. 8 that the higher order nonlinearity provides effective optical limiting at fluences where the multiphoton processes dominate.

The principal advantage of the lead phenanthralocyanine, **5c**, is the broad transmission window in the visible and a relatively neutral light olive color to the eye. The initial nonlinear optical response is primarily attributed to a thermorefractive response, a thermal change in the index of refraction. The thermorefractive response can provide optical limiting. The optical limiting at moderate fluences is similar to that found in other limiters based on

the thermorefractive effect, but it is not as good as a tetrakis-cumylphenoxy phthalocyanine limiter [14] which has a 50 mJ/cm² threshold.

Improving the threshold of the Pb phenanthralocyanine optical limiter could be achieved by reducing the internal conversion rate of the initially excited state. The fast internal conversion time might be due to the distortion of the ring from planarity. Interconversions between the different low lying conformations could provide a mechanism to enhance internal conversion. Alternatively, intermolecular interactions in the pure liquid material could also contribute to a fast internal conversion. Aggregation can increase the relaxation rate of an excited state but is probably not important here [14]. Introducing bulkier peripheral groups to the phenanthralocyanine structure could inhibit either of these the fast relaxation processes.

SUMMARY

Phenanthralocyanine compounds with cumyl-phenoxy, nonylphenoxy and dimethylsiloxane oligomer peripheral substitution were synthesized and characterized. The latter two compounds were soluble in common organic solvents, and the siloxane product was an isotropic liquid. Compared with the phthalocyanine analog, the Q bands of the Pb, H_2 and Cu phenanthralocyanine were slightly red shifted and variably broadened (small for PbPhc but large for H_2Phc and CuPHc). The nominal red shift is a consequence of an angular annelation of the benzene rings to the phthalocyanine system. Aggregation was not detected in toluene solution, and the Q band broadening was attributed to distortion of the tetraazaporphyrin ring to nonplanar conformations. Nonlinear optical measurements were performed on the siloxane substituted lead phenanthralocyanine neat liquid to evaluate it as an optical limiting material. In pure thin film form this material has a desirable, broad transmission window in the visible spectrum and a relatively neutral light olive color to the eye. The first nonlinear optical response at fluences of a few mJ/cm² is primarily a thermorefractive response, a change in the index of refraction. The refractive changes arise because a large fraction of the absorbed light appears as local heating within a few picoseconds. The threshold for such thermorefractive limiting occurs at a higher fluences than the phthalocyanine systems where the predominate contribution is reverse saturable absorption. While the contribution from nonlinear absorption (reverse saturable absorption) is small initially, a strong, higher order, nonlinear absorption was observed at fluences greater than 100 mJ/cm². This new mechanism gives very efficient optical limiting at higher fluences.

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"Synthesis, Aggregation Behavior and Nonlinear Absorption Properties of Lead Phthalocyanines Substituted with Siloxane Chains"
E.M. Maya, A.W. Snow, J.S. Shirk, R.G.S. Pong, S.R. Flom and G.L. Roberts
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Synthesis, aggregation behavior and nonlinear absorption properties of lead phthalocyanines substituted with siloxane chains

Eva M. Maya,[a,b] Arthur W. Snow,[a] James S. Shirk,[c] Richard G. S. Pong,[c]
~~Stoven D. Flom,[c] and Goodd L. Dol. et.[b]~~

[a]Naval Research Laboratory, Chemistry Division Code 6120, Washington DC 20375-5342, USA
[b]George Mason University, Department of Chemistry, 4400 University Drive, Fairfax, Virginia 22030-4444, USA
[c]Naval Research Laboratory, Optical Sciences Division Code 5613, Washington DC 20375-5338, USA

The synthesis and characterization of polysiloxane substituted metal-free and lead phthalocyanines are described. These materials form a class of isotropic liquid phthalocyanines that combine a large nonlinear absorption with an exceptionally large nonlinear thermal refractive effect. These materials effectively couple the nonlinear absorption characteristics of the phthalocyanine (Pc) moiety with the thermorefractive properties typical of siloxanes. The room temperature index of these phthalocyanines can be varied by the choice of the siloxane substituent. Furthermore, the siloxane substituents are effective at inhibiting aggregation of the phthalocyanine rings. The observed aggregation constants in toluene solutions are very small and only a small degree of aggregation is observed even in the pure liquid phthalocyanines. Nonlinear transmission, z-scan, transient absorption and degenerate four-wave mixing studies confirm that the Pb substituted materials possess a broad spectral region of induced absorption with nonlinear absorption coefficients similar to that observed from other lead substituted phthalocyanines. The observed ground state molar absorption coefficients of the siloxy phthalocyanines are somewhat smaller than comparable alkyl substituted phthalocyanines. Taken together, these properties make these materials very useful for practical nonlinear optical applications. The coupling of siloxane chains to the Pc rings represents a promising way to achieve some important properties that are difficult to achieve by other means.

Introduction

One of the goals of materials science and chemistry is to incorporate new functionalities into existing materials without altering the fundamental response mechanisms that made the material originally interesting. This paper describes a realization of that goal. We have recently synthesized a series of polysiloxane phthalocyanines that were specifically designed to possess useful nonlinear optical properties. In addition to their nonlinear optical properties, these materials are designed to be viscous, thermorefractive, isotropic liquids that form optically clear thin films, which facilitates their use in practical optical applications.

While the materials described in this paper were designed to possess enhanced nonlinear optical and optical limiting responses, the unique properties of these new materials may prove useful in other applications. In addition to being among the best nonlinear materials for optical limiting applications,[1–3] phthalocyanines are an important class of commercial dyes and coloring agents. They have been used as laser dyes,[4] as photoreceptors in color copiers and color laser printers and as a photoactivator in several brands of CD-R discs.

Optical limiters are nonlinear optical devices whose transmission decreases with increasing applied intensity. These devices require materials with appropriate nonlinear optical response mechanisms, in particular nonlinear absorption and nonlinear refraction. The nonlinear absorption properties of many dyes have been investigated.[5] It has been found that materials that have higher absorption cross sections in the excited state than they do in their ground state yield positive nonlinear absorption coefficients. This effect is sometimes called reverse saturable absorption (RSA). A number of dye materials, primarily phthalocyanines and porphyrins, with large positive nonlinear absorption coefficients have been reported. The desirability of materials with a large intensity or fluence dependent refractive index in such applications has been recognized.[5–7] We know of few examples of materials that are strong nonlinear absorbers and also possess a large nonlinear refractive index. In most previous cases the refractive response was dominated by that of the solvent. An intrinsic, fluence dependent refractive index is desirable when the nonlinear material is used pure or as a thin film.

The peripherally substituted silicone phthalocyanines (Pc's) reported here combine large nonlinear absorption and nonlinear refraction coefficients. The source of the fluence dependence of the refractive index is thermal. Our hypothesis is that the silicone-substituted phthalocyanines can couple the large refractive index variation with temperature (dn/dT) characteristic of the siloxane structure[8] with the large nonlinear absorption (reverse saturable absorption) characteristic of the phthalocyanine ring.[1]

In addition to the nonlinear response characteristics, these silicone phthalocyanines possess other useful properties: optical transparency over a relatively broad region, photo-oxidative stability, as evidenced by the invariance of the UV-vis absorption spectrum over a period of months, and processability as a solution, glass or liquid. In previous materials, some of these properties have been achieved. Peripheral substitution of arylethers at the phthalocyanine ring,[5,9] for example, introduction of cumylphenoxy substituents, generates effective optical limiting materials with excellent solubility and photooxidative stability.[1] However, this material is a solid in pure

form and does not readily form transparent films. The introduction of an alternative peripheral substituent group, phenylglycidylether, allowed the formation of optically clear thin films of the pure material.[10] These thin films are glassy and were found to have relatively low damage thresholds.[11] Attachment of ethyleneoxide oligomer substituents to the Pc core, yields intrinsic liquids which also form optically clear

Unfortunately, the material with the best nonlinear absorption characteristics, a lead substituted version, was found to be unstable upon dilution in common solvents.

Another important feature in phthalocyanine design for nonlinear optical applications is the control over aggregation. Phthalocyanines tend to form aggregates in solution and films. Aggregation reduces the excited state lifetime and hence the effective nonlinear optical absorption coefficients. Strategies to reduce aggregation include incorporation of long alkyl chains in the α position of the phthalocyanine ring[12-15] or substitution at the β position with bulky groups such as large dendritic substituents.[16] We postulated that the substitution of the Pc ring with poly(dimethylsiloxane) chains (10 repeat units length) would also be effective for suppression of aggregation in solution.[7]

In this paper the preparation and properties of some peripheral silyloxy substituted phthalocyanines and their lead substituted analogs are described in detail. We show that silyloxy substitution gives a novel class of isotropic liquid phthalocyanines with an exceptionally large thermorefractive effect combined with a large nonlinear absorption. Aggregation studies of these compounds are reported and preliminary data on the nonlinear optical properties are given. The synthesis of a lead phthalocyanine with phenyl substituted siloxane chains is also described to demonstrate the variability of the linear refractive index of the material. The coupling of siloxane chains to the Pc rings represents a promising way to achieve some important properties that are difficult using more common substituents.

Experimental

General

Reagents (Gelest, Aldrich, Fisher) were used without further purification unless otherwise noted. Dry THF were used after refluxing under nitrogen over lithium aluminium hydride and distillation just prior to use. Chromatographic purifications were performed on silica gel columns (Fluka AG 60, activity 2–3). NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). Deuterated acetone or chloroform were used as solvents, and the chemical shifts are internally referenced to CD_3COCD_3 (2.04 and 29.8 ppm) or to $CDCl_3$ (7.26 and 77 ppm) for the respective ^{1}H and ^{13}C nuclei. Infrared spectra were obtained from samples deposited as thin films on NaCl plates and the spectra were recorded using a Nicolet Magna FTIR 750. UV-VIS spectra were measured using either a Perkin Elmer Lambda 5 or Lambda 9 spectrophotometer. Differential scanning calorimetry (DSC) data were recorded on a DuPont 2100 thermal analysis system/910 DSC module. Melting points were determined in an electro-thermal melting point apparatus and are uncorrected. Refractive indices of colorless compounds were measured with a Bausch & Lomb Abbe-3L refractometer (589 nm; 20 °C) and those of phthalocyanine compounds were measured via both a Woolam spectroscopic ellipsometer and a Metricon Model 2010 prism coupler.

The experimental apparatus for the nonlinear optical characterization has been described.[3] Briefly, the laser source for the nanosecond experiments was an optical parametric oscillator (Continuum Surelite) pumped by the third harmonic of a Nd/YAG laser. The pulse width of this laser was 2.5

nanoseconds. Some of the nanosecond experiments at 532 nm used a doubled Nd/YAG (Spectra-Physics) laser with a pulse width of 8 nanoseconds. The beam was spatially filtered and the experiments were performed used f/5 focusing optics. The experiments were conducted at 10 Hz for lower fluences but at higher fluences, where persistent thermal effects are possible, the repetition rate was reduced to 0.5 Hz. At the highest ...., ... each data point was on a fresh sample. The picosecond time resolved experiments included degenerate four-wave mixing (DFWM) studies and spectrally resolved transient absorption. They were performed using a dye laser that is synchronously pumped by the second harmonic of a CW mode-locked Nd:YAG laser. The dye laser output is amplified in a three-stage dye amplifier pumped by the second harmonic of a regenerative Nd:YAG amplifier seeded with the fundamental of the mode-locked Nd:YAG laser. The 10 Hz output of this laser system provides 1.2 ps FWHM pulses with energies up to 1 mJ. For these experiments the laser system was tuned between 589–606 nm.

Synthetic procedures

4-(2-allylphenoxy)phthalonitrile, 3. To a 250 mL two-neck flask fitted with a magnetic stirring bar and nitrogen inlet tube, was added 25 mL of Me_2SO, 5 g (0.028 mol) of 4-nitro-phthalonitrile (1) and 3.94 g (0.029 mol) of 2-allylphenol (2). The mixture was stirred at room temperature while 6.57 g (0.047 mol) of anhydrous potassium carbonate were added in 0.54 g quantities at 0.5 h intervals over a 6 h period. The reaction mixture was stirred overnight under nitrogen. The reaction was worked up by filtering and concentrating at reduced pressure to near dryness. The brown oil obtained was extracted with 100 mL CH_2Cl_2 and washed twice with 100 mL of water. The CH_2Cl_2 phase was separated and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the oil was passed through an alumina column using toluene elution. Yield 4.45 g (61%). M.p = 49–51 °C; ^{1}H NMR ($CDCl_3$) δ ppm 3.23 (2H, d, CH_2), 4.95 (2H, dd, =CH_2), 5.78 (1H, m, =CH), 6.95 (1H, d, H_{arom}), 7.12–7.33 (5H, m, H_{arom}), 7.68 (1H, d, H_{arom}); ^{13}C NMR ($CDCl_3$) δ ppm 34.0, 108.5, 114.9 and 115.4 (CN), 116.7, 117.6, 120.8, 120.9, 121.0, 126.7, 128.5, 131.6, 132.4, 135.3, 135.4, 151.1, 161.7; IR (NaCl) ν cm^{-1} 3082 (=CH_2), 2229 (CN), 1615 (C=C), 1595 and 1486 (C–C), 1246 (C–O–C).

Butyl capped hydrosilyl terminated polydimethylsiloxane (PDMS) oligomers, 5a–b. The procedure was adopted from Holohan et al.[17] A solution of hexamethylcyclotrisiloxane (4a) in THF (33% w/v) was prepared by passing 6 g (0.027 mol) of hexamethylcyclotrisiloxane through an alumina column under nitrogen. Dry THF was passed through the column until 18 g of solution was collected in a preflamed flask equipped with a magnetic stirring bar placed at the end of the column. The flask was immediately closed and immersed in an ice–water bath. A solution of BuLi in hexane was added with stirring. For compound 5a 3.59 mL (9 mmol) of BuLi were used, and for compound 5b 1.79 mL, (4.5 mmol) were used. After initiation, the polymerization was allowed to proceed at room temperature for between 15 and 20 h. The reaction was terminated by the slow addition of chlorodimethylsilane at −78 °C (for 5a 4 mL (0.036 mol) $(CH_3)_2SiHCl$ and for 5b 2 mL (0.018 mol) $(CH_3)_2SiHCl$). This mixture was stirred for 30 min at −78 °C and two hours at room temperature during which time a precipitate of LiCl formed. THF, hexane and excess chloro-dimethylsilane were removed by rotary evaporation. LiCl was then removed by filtration. Further purification of the oligomer was carried out by heating under vacuum at 120 °C.

5a (Bu^n-PDMS$_{10}$-H). Yield: 5.50 g (78%); $Tg = -134$ °C; $n_D = 1.4008$; ^{1}H NMR (D$_3$CCOCD$_3$) δ ppm 0.05 (6H, d, -SiCH$_3$), 0.19 (54H, m, -SiCH$_3$), 0.53 (2H, m, CH$_2$), 0.89 (3H, t, CH$_3$), 1.32 (4H, m, CH$_2$), 4.70 (1H, q, SiH); IR (NaCl) v cm^{-1} 2972.2 (CH), 2132 (SiH), 1272 (SiCH$_3$), 1098 and 1027 (SiOSi), 800 (SiC).

$n_D = 1.4020$; ^{1}H NMR (D$_3$CCOCD$_3$) δ ppm 0.07 (114H, m, -SiCH$_3$), 0.58 (2H, m, CH$_2$), 0.89 (3H, t, CH$_3$), 1.37 (4H, m, CH$_2$), 4.71 (1H, q, SiH); IR (NaCl) v cm^{-1} 2970 (CH), 2132 (SiH), 1266 (SiCH$_3$), 1104 and 1033 (SiOSi), 807 (SiC).

Butyl capped hydrosilyl terminated polymethylphenylsiloxane, 5c (Bu^n-PMPhS$_{10}$-H). A solution of trimethyltriphenylcyclotrisiloxane (4b) in THF (33% w/v) was prepared by passing 7 g (0.017 mol) of trimethyltriphenylcyclotrisiloxane through an alumina column under nitrogen. Dry THF was passed through the column until 21.2 g of solution were collected in a preflamed flask equipped with a magnetic stirring bar placed at the end of the column. The flask was immediately closed and immersed in an ice–water bath. A 2.5 M solution of BuLi in hexane (2.25 mL, 5.6 mmol) was added with stirring. After initiation, the polymerization was allowed to proceed at room temperature for between 15 and 20 h. The reaction was terminated by the slow addition of 2.55 mL (0.022 mol) of (CH$_3$)$_2$SiHCl at -78 °C. This mixture was stirred for 30 min at -78 °C and two hours at room temperature during which time a precipitate of LiCl formed. THF, hexane and excess chlorodimethylsilane were removed by rotary evaporation. LiCl was then filtered. The product was further purified by heating under vacuum at 120 °C to yield 4.51 g (60%) of colorless oil. $Tg = -69$ °C; $n_D = 1.5255$; ^{1}H NMR (D$_3$CCOCD$_3$) δ ppm 0.11–0.55 (33H, m, -SiCH$_3$), 0.83 (5H, m, -CH$_3$, CH$_2$), 1.31 (4H, m, CH$_2$), 4.77 (1H, q, SiH), 7.19–7.69 (45H, m, H$_{arom}$); IR (NaCl) v cm^{-1} 3069, 2972 and 2897 (CH), 2125 (SiH), 1595 and 1440 (SiPh), 1259 (SiCH$_3$), 1130 and 1072 (SiOSi), 910 (SiC), 794 and 729 (PhSi CH$_3$).

Butyl capped polysiloxane methylene phenoxy phthalonitriles, 6a–c. *General procedure.* To a flask equipped with a magnetic stirring bar were added 1 g (3.85 mmol) of 2-allylphenoxyphthalonitrile 3 and 3 drops of a 0.1 M solution of hydrogen hexachloroplatinate(IV) hydrate (H$_2$PtCl$_6$) in isopropanol. The mixture was heated at 60 °C and 3.85 mmol of the corresponding butyl capped hydrosilyl terminated polysiloxane oligomer (5a–c) were added followed by 1 h stirring. The light brown oil obtained was purified by column chromatography on silica with toluene as the eluent to give a colorless oil.

6a. Yield: 1.40 g (35%); $Tg = -111$ °C; $n_D = 1.4482$; ^{1}H NMR (D$_3$CCOCD$_3$) δ ppm 0.012–0.064 (60H, m, -SiCH$_3$), 0.54 (4H, m, -SiCH$_2$), 0.86 (3H, t, CH$_3$), 1.29 (4H, m, CH$_2$), 1.58 (2H, m, CH$_2$), 2.49 (2H, t, CH$_2$), 6.95 (1H, d, H$_{arom}$), 7.14–7.31 (5H, m, H$_{arom}$), 7.68 (1H, d, H$_{arom}$); ^{13}C NMR (D$_3$CCOCD$_3$) δ ppm 0.37 (Si(CH$_3$)$_2$C), 1.39 (OSi(CH$_3$)$_2$O), 14.08 (CH$_3$), 18.51 and 18.71 (SiCH$_2$), 23.90, 24.80 and 26.9 (CH$_2$), 34.1 (PhCH$_2$), 109.22 and 115.85 (C$_{arom}$), 116.26 (CN), 118.21, 121.90, 121.99, 122.08, 127.19, 128.90, 132.29 (CH$_{arom}$), 135.50 (C$_{arom}$), 136.81 (CH$_{arom}$), 155.12 and 161.08 (C–O–C); IR (NaCl) v cm^{-1} 2959 (CH), 2234 (CN), 1608 and 1492 (C–C), 1259 (SiCH$_3$), 1098 and 1033 (SiOSi), 806 (SiC).

6b. Yield: 3.49 g (53%); $Tg = -122$ °C; $n_D = 1.4317$; ^{1}H NMR (D$_3$CCOCD$_3$) δ ppm 0.016–0.084 (114H, m, -SiCH$_3$), 0.54 (4H, m, -SiCH$_2$), 0.88 (3H, t, CH$_3$), 1.32 (4H, m, CH$_2$), 1.55 (2H, m, CH$_2$), 2.50 (2H, t, CH$_2$), 6.95 (1H, d, H$_{arom}$), 7.15–7.32 (5H, m, H$_{arom}$), 7.70 (1H, d, H$_{arom}$); ^{13}C NMR (D$_3$CCOCD$_3$) δ ppm 0.55 (Si(CH$_3$)$_2$C), 1.54 (OSi(CH$_3$)$_2$O), 13.80 (CH$_3$), 17.96 and 18.19 (SiCH$_2$), 24.01, 25.46 and 26.38 (CH$_2$), 33.53 (PhCH$_2$), 108.53 and 114.97 (C$_{arom}$), 115.40 (CN), 117.73, 120.75, 121.02, 126.65, 128.06 and 131.57

(CH$_{arom}$),134.86 (C$_{arom}$), 135.40 (CH$_{arom}$), 151.29 and 162.03 (C–O–C); IR (NaCl) v cm^{-1} 2966 (CH), 2235 (CN), 1608 and 1492 (C–C), 1272 (SiCH$_3$), 1098 and 1033 (SiOSi), 800 (SiC).

6c. Yield: 4.43 g (72%); $Tg = -42$ °C; $n_D = 1.5398$; ^{1}H NMR (D$_3$CCOCD$_3$) δ ppm 0.13–0.52 (m, -SiCH$_3$), 0.91 (m, CH$_3$), 1.24 (m, CH$_2$), 1.65 (m, CH$_2$), 2.50 (m, CH$_2$), 7.21–7.88 (m, H$_{arom}$); ^{13}C NMR (D$_3$CCOCD$_3$) δ ppm 0.17 (Si(CH$_3$)$_2$C), ... (......), ... (CH$_3$), ... and 16.63 (SiCH$_2$), 24.69, 26.03 and 26.93 (CH$_2$), 34.43 (PhCH$_2$), 109.17 and 115.93 (C$_{arom}$), 116.35 (CN), 127.20, 128.52, 128.65, 128.90, 130.17, 130.51, 130.60, 132.31, 133.95, 134.05 and 134.13 (CH$_{arom}$), 135.44 (C$_{arom}$), 136.82 (CH$_{arom}$), 152.51 and 162.82 (C–O–C); IR (NaCl) v cm^{-1} 3076, 2966 and 2869 (CH), 2242 (CN), 1602, 1505 and 1427 (SiPh), 1266 (SiCH$_3$), 1136 and 1085 (SiOSi), 807 (SiC), 790 and 730 (PhSiCH$_3$).

Tetra(butyl capped polysiloxane methylene phenoxy) lead phthalocyanines, 7a–c. *General procedure.* A 10 × 75 mm tube was charged with 0.5 mmol of the corresponding butyl capped polysiloxane methylene phenoxy phthalonitrile (6a–c), 0.082 g (0.37 mmol) of yellow PbO (Fisher) and a stirring bar, degassed under vacuum (~1 torr) with gentle warming (5 min), sealed under vacuum and heated at 165–170 °C with stirring for 12 h. In the case of phthalonitrile 6c, the reaction was maintained for 48 h. The crude product was dissolved in 10 mL of toluene filtered and purified by passing through a silica column with toluene elution. The first fractions were contaminated with a triazine byproduct[18] and discarded. Subsequent fractions were concentrated and vacuum dried (2 h at 80 °C) to yield a green liquid.

7a (PbPc(Bu^{n}PDMS$_{10}$)$_4$). Yield: 0.220 g (40%); $Tg = -122$ °C; UV (toluene) λ nm 721, 648, 365; IR (NaCl) v cm^{-1} 2959 (CH), 1608 and 1492 (C–C), 1253 (SiCH$_3$), 1091 and 1014 (SiOSi), 800 (SiC).

7b (PbPc(Bu^{n}PDMS$_{19}$)$_4$). Yield: 0.317 g (36%); $Tg = -121$ °C; UV (toluene) λ nm (ε) 719 (84947), 648 (17845), 365 (27415); IR (NaCl) v cm^{-1} 2966 (CH), 1621 and 1486 (C–C), 1266 (SiCH$_3$), 1091 and 1033 (SiOSi), 800 (SiC).

7c (PbPc(Bu^{n}PMPhS$_{10}$)$_4$). Yield: 0.372 g (45%); $Tg = -46$ °C; UV (toluene) λ nm (ε) 719 (2.9 × 10^4), 646 (5.8 × 10^3), 368 (8.5 × 10^3); IR (NaCl) v cm^{-1} 3069, 2966 and 2869 (CH), 1610, 1595 and 1427 (SiPh), 1266 (SiCH$_3$), 1130 and 1085 (SiOSi), 794 (SiC), 730 and 720 (PhSiCH$_3$).

Tetra(butyl capped polysiloxane methylene phenoxy) metal free phthalocyanine, 8. Two drops of trifluoroacetic acid were added to a solution of 0.100 g of lead phthalocyanine PbPc(Bu^{n}PDMS$_{10}$)$_4$ in 5 mL of CH$_2$Cl$_2$ followed by 10 min stirring at 20 °C. The CH$_2$Cl$_2$ solution was extracted twice with 10 mL of 5% Na$_2$CO$_3$, washed twice with distilled water and dried (anh MgSO$_4$) to yield 0.081 g (85%) of a blue liquid. $Tg = -115$ °C; UV (toluene) λ nm 703, 666, 638, 605, 346; IR (NaCl) v cm^{-1} 3295 (NH), 2959 (CH), 1615 and 1479 (C–C), 1259 (SiCH$_3$), 1091 and 1027 (SiOSi), 807 (SiC); MS m/z 4500–2200.

Tetraallylphenoxy lead phthalocyanine, 9. A 10 × 75 mm tube was charged with 0.500 g (1.92 mmol) of allylphenoxy phthalonitrile (3), 0.329 g (1.47 mmol) of PbO (Fisher) and a stirring bar, degassed under vacuum (~1 torr) with gentle warming (5 min), sealed under vacuum and heated at 165–170 °C with stirring for 12 h. The crude product was dissolved in 10 mL of CH$_2$Cl$_2$, filtered and purified by passing through an alumina column (ICN EcoCrom, activity 1) with CH$_2$Cl$_2$ elution. The first fractions were contaminated with a triazine byproduct[18] and discarded. Subsequent fractions were concentrated and vacuum dried (2 h at 80 °C) to yield a green solid. Yield; 0.61 g (42%); mp > 300 °C; UV (toluene) λ nm 721, 650, 346; IR (NaCl) v cm^{-1} 3076 (=CH$_2$), 2919 (CH), 1638 (C=C), 1608, 1485 (C–C), 1239 (C–O–C).

Tetraallylphenoxy metal free phthalocyanine, 10. A 10 × 75 mm tube was charged with 0.500 g (1.92 mmol) of allylphenoxy phthalonitrile (3), 0.052 g (0.48 mmol) of hydroquinone and a stirring bar, degassed under weak vacuum (~20 torr/5 min), sealed under vacuum and heated at 165–170 °C with stirring for 12 h. The crude product was dissolved in 10 mL of CHCl₃, filtered and purified by passing through an alumina column (ICN EcoCrom, activity 1) with CHCl₃ elution, concentrated and precipitated into methanol to yield a blue solid. This compound can also be prepared by displacement of the lead ion following the procedure described for the synthesis of the metal free phthalocyanine $H_2Pc(Bu^nPDMS_{10})_4$. Yield; 0.293 g (56%); mp > 300 °C; ^1H NMR (CDCl₃) δ ppm −4.1 (s, NH), 3.6 (m, CH₂), 5.1 (m, =CH₂), 6.1 (m, CH=), 6.8–7.7 (m, H-arom); UV (toluene) λ nm 703, 667, 639, 605, 350; IR (NaCl) ν cm⁻¹ 3295 (NH), 3075 (=CH₂), 1638 (CH=CH₂), 1611 and 1467 (C–C), 1228 (C–O–C); MS m/z 1091.

Results and discussion

Synthesis and characterization

The peripherally substituted siloxane phthalocyanines PbPc-$(Bu^nPDMS_{10})_4$, PbPc$(Bu^nPDMS_{19})_4$ and PbPc$(Bu^nPMPhS_{10})_4$ were synthesized according to Scheme 1.

In the first step the base-catalyzed nucleophilic aromatic nitro displacement[19] of 4-nitrophthalonitrile (1) with 2-allylphenol afforded 4-(2-allylphenoxy)phthalonitrile, (3), and the butyl capped hydrosilyl terminated poly(dimethyl-siloxane) (Bu^n-PDMS-H) oligomers (5a,b) were synthesized by an anionic ring opening polymerization of hexamethylcyclo-trisiloxane (D₃) (4a) with butyl lithium (BuLi).[17] To obtain PDMS oligomers ... were carried out using 3:1 or 6:1 mole ratios of D₃ and BuLi. The butyl capped methylphenyl oligomer 5c was prepared by using a 3:1 molar ratio of trimethyltriphenylcyclotrisiloxane (4b) and BuLi. All reactions were terminated by the slow addition of chlorodimethylsilane. The number average chain length of the PDMS and PMPhS oligomers and their hydrosilyl group functionality were determined from the ^1H NMR spectroscopy integrals of the butyl, hydrosilyl and silylmethyl proton resonances. A 1:1 butyl:hydrosilyl ratio was obtained for each oligomer, and the oligomer chain lengths determined are consistent with those calculated from the Holohan reference. The butyl capped hydride terminated siloxane oligomers (5a–b) were then coupled to the 4-(2-allylphenoxy)-phthalonitrile 3 by a hydrosilylation reaction using hydrogen hexachloroplatinate hydrate (H_2PtCl_6) as catalyst. The reaction's progress was followed spectroscopically (IR and ^1H
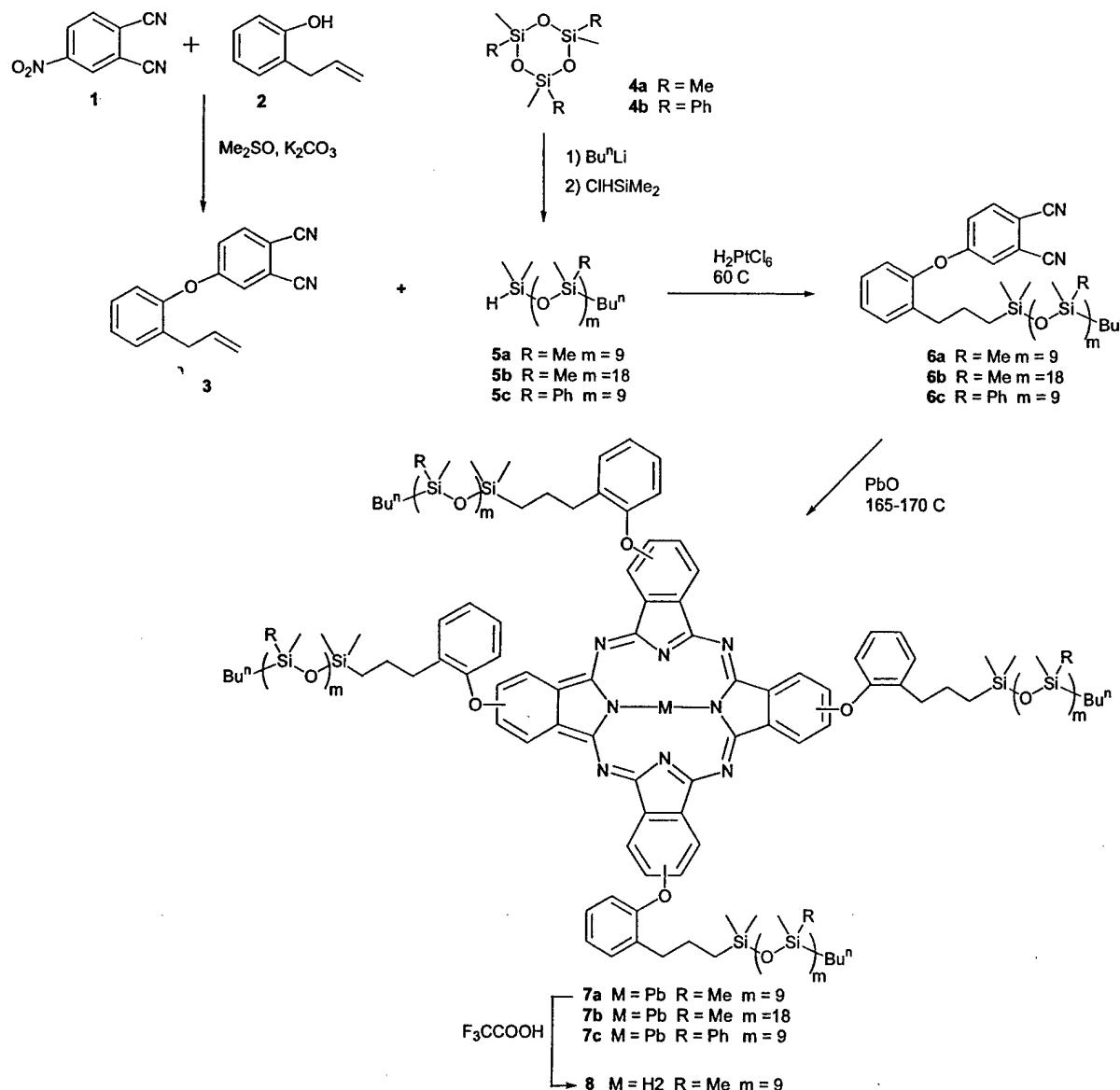
Scheme 1 Preferred PbPc$(Bu^nPDMS_m)_4$ synthesis route.

NMR) by disappearance of the Si-H (2128 cm^{-1}; 4.70 ppm) and allyl (1615 cm^{-1}; 3.23, 4.95 and 5.78 ppm) functional groups.

In the next step, the butyl capped siloxane lead phthalocyanines (7a–c) were prepared by reacting the corresponding phthalonitriles (6a–c) with a stoichiometric quantity of lead oxide in a sealed tube.[20,21] In addition to phthalocyanine formation, small amounts of tris(phenyloxyano)triazine were obtained in all cases as a by-product.[16] The triazine derivatives were easily detected by IR (a weak -CN absorption at 2221 cm^{-1} and strong triazine ring absorptions at 1520 and 1360 cm^{-1}). The phthalocyanines were purified by column chromatography on silica gel using toluene elution. The IR spectra of the purified lead phthalocyanines PbPc(Bu^{n}PDMS$_{10}$)$_4$, PbPc(Bu^{n}PDMS$_{19}$)$_4$ and PbPc(Bu^{n}PMPhS$_{10}$)$_4$ were free of the triazine and phthalonitrile precursor (2234 cm^{-1}) bands and displayed the bands associated with the dimethylsiloxane structure (1253 cm^{-1} Si-CH$_3$ symmetric deformation, 1091 and 1014 cm^{-1} Si-O-Si stretching vibrations and 800 cm^{-1} Si-C stretching and CH$_3$ rocking). The IR spectrum of the PbPc(Bu^{n}PMPhS$_{10}$)$_4$ displayed additional bands due to the phenyl groups attached to the siloxane chain (1610, 1595 and 1427 cm^{-1} Si-Ph stretching and 730 and 720 cm^{-1} Ph-Si-CH$_3$ stretching).

NMR spectra are particularly useful in monitoring the transformations of the allylphenoxyphthalonitrile 3 to the n-butyl terminated siloxane functionalized phthalonitrile 6 and subsequently to the phthalocyanine analog 7. The spectra also provide a good internal stoichiometry check between the siloxane chain and the phthalonitrile or phthalocyanine structures and an observation of phthalocyanine ring current effects on peripheral structures. As an example, spectra of the transformations of 3 to 6a to 7a are presented in Fig. 1. The allyl group in 3 is transformed via the hydrosilylation reaction to the trimethylene group in 6a as represented by the a, b, c peak assignments. This transformation also attaches an n-butyl terminated polydimethylsiloxane chain. Integration of resonances assigned to the n-butyl group (d, e, f, g) are consistent with a 1:1 stoichiometry with the trimethylene group as required by the structure of 6a. Transformation of 6a to the phthalocyanine 7a results in a broadening and shifting of the aromatic resonances as well some of the aliphatic resonances. The broadening and shifting is most pronounced for the protons situated closest to the phthalocyanine ring. The broadening is due to a mixed isomer character of the phthalocyanine compound and to longer relaxation times associated with the larger rigid structure. Di-substitution substituted at the 4-position generate four possible phthalocyanine isomers, and these have recently been separated with respective NMR assignments made.[22] The downfield shifting is attributable to the phthalocyanine ring current effect with the stronger effects being observed on the aromatic proton resonances (a' and b') although shifting is also observed for the trimethylene resonances. Similar effects were also observed for ethyleneoxide oligomer substituted phthalocyanine compounds.[23]

The lead ion complexed in the phthalocyanine cavity is not stable toward conditions for mass spectral analysis. In order to obtain mass spectral characterization of the phthalocyanine with this peripheral structure, the metal free phthalocyanine H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ was also prepared by treatment of the corresponding lead Pc, PbPc(Bu^{n}PDMS$_{10}$)$_4$, with trifluoroacetic acid. The mass spectrum of this compound is consistent with the assigned structure[7] and consists of peaks separated by 74 amu due to -Si(CH$_3$)$_2$O- degradation which is characteristic of the mass spectra of PMDS oligomers.[24]

As further confirmation of product, an alternative route wherein phthalocyanine formation occurs prior to attachment of the peripheral silicone pendant groups was followed (Scheme 2). In this scheme, the tetrakis(allylphenoxy) lead phthalocyanine 9 is prepared by cyclotetramerization of 4-(2-allylphenoxyphthalonitrile) 3 in the presence of lead oxide[20,21] in a sealed tube. In the second step the hydrosilylation reaction was conducted using an excess of oligomer 5a and platinum-divinyl tetramethylsiloxane complex as catalyst to yield the Bu^n-PDMS lead phthalocyanine PbPc(Bu^{n}PDMS$_{10}$)$_4$. This route can also be used to prepare the corresponding Bu^n-PDMS metal free phthalocyanine by hydrosilylation reaction over the tetrakis(allylphenoxy) metal free phthalocyanine (10).
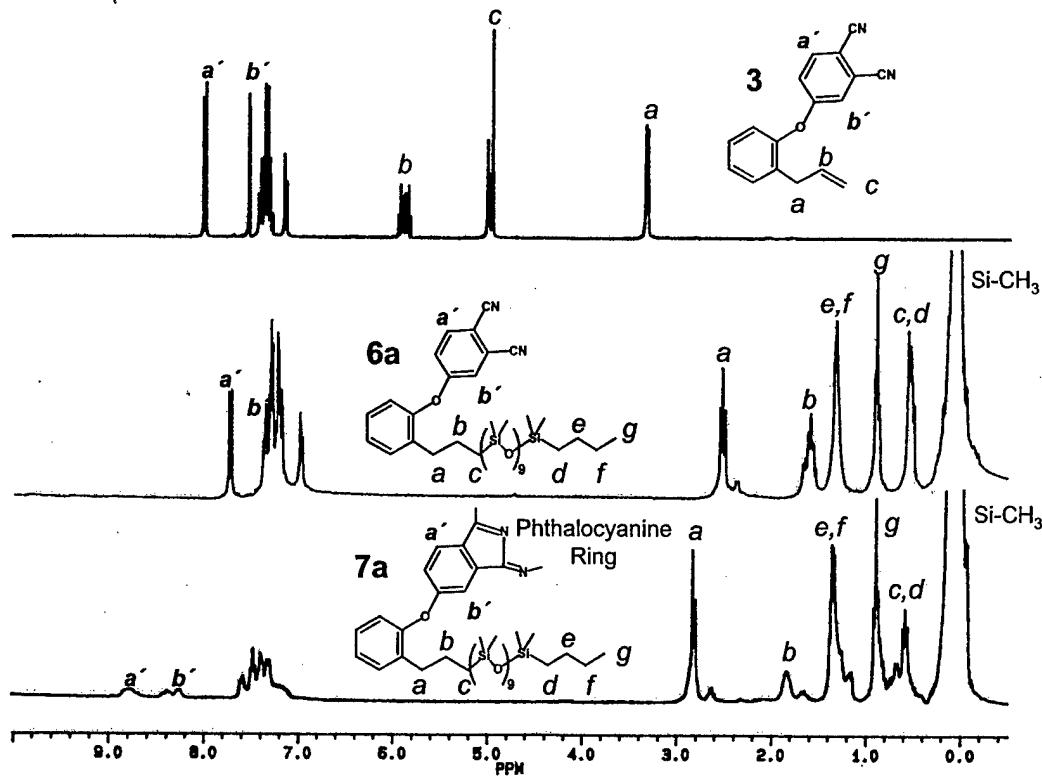
Fig. 1 NMR spectra of compounds 3, 6a and 7a. The resonance assignments shown are discussed in the text.

for 9
PbO, 165-180 C
for 10
Hydroquinone, 165-170 C

Platinum-divinyl tetramethyl-
disiloxane

7a or 8

9 M = Pb
10 M = H2
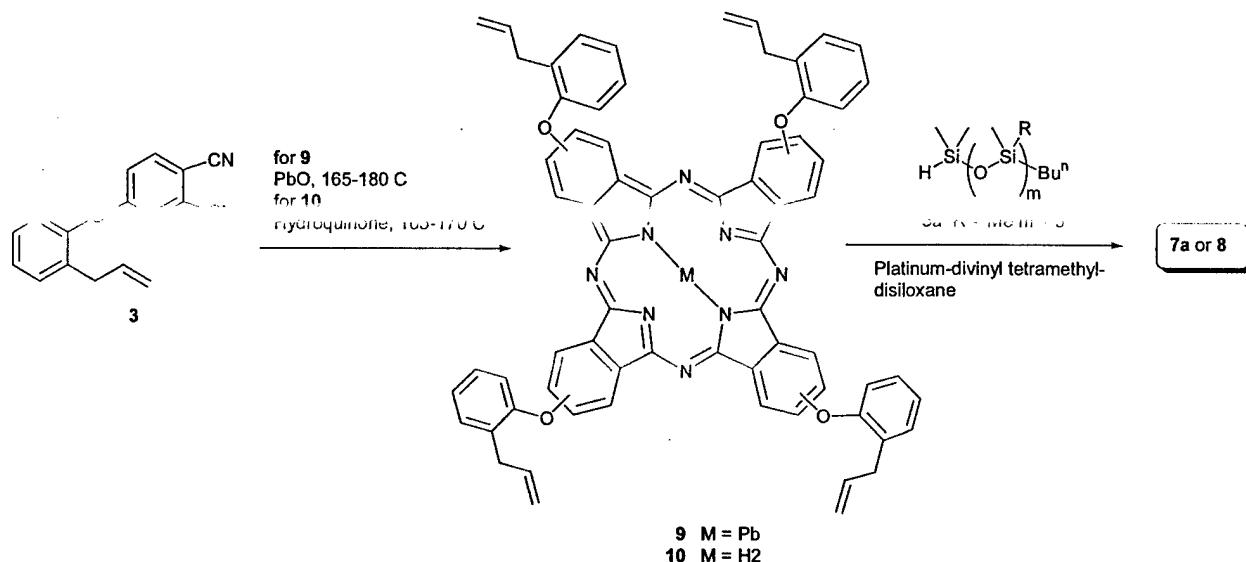
Scheme 2 Alternative PbPc(Bu^{n}PDMS$_m$)$_4$ synthesis route.

This phthalocyanine was prepared by reacting the corresponding phthalonitrile **3** with a stoichiometric quantity of hydroquinone in a sealed tube.[18] This second route has the disadvantage of a more arduous purification because of the required excess of oligomer **5a** to ensure the conversion of all allyl groups. In addition, a heterogeneous non-acidic catalyst is necessary to avoid the displacement of the lead ion.

The success of the methods developed lie in the use of butyl capped hydride terminated oligomers (**5a–c**) instead of commercial α,ω-dihydride terminated PDMS. We have observed when using commercial dihydride terminated oligomers,[25] polymeric species can be formed due to the coupling tendency of the Si–H group which makes the synthesis, purification and handling more difficult.

Fig. 2 shows the UV-vis spectra of dilute toluene solutions of the new PbPc's PbPc(Bu^{n}PDMS$_{10}$)$_4$, PbPc(Bu^{n}PDMS$_{19}$)$_4$ and PbPc(Bu^{n}PMPhS$_{10}$)$_4$. All three compounds display a Q-band characteristic of lead phthalocyanine in both shape and wavelength maximum (719 nm). Molar absorption coefficients (ε) obtained for the polydimethylsiloxane lead phthalocyanines PbPc(Bu^{n}PDMS$_{10}$)$_4$ and PbPc(Bu^{n}PDMS$_{19}$)$_4$ are 0.79 and 0.80 × 10^5 l mol^{-1} cm^{-1} respectively. The polymethylphenylsiloxane lead phthalocyanine PbPc(Bu^{n}PMPhS$_{10}$)$_4$ shows a lower molar absorption coefficient of 0.3 × 10^{-5} l mol^{-1} cm^{-1}. All values are somewhat smaller than those reported for phthalocyanines containing other peripheral oligomer pendant

groups such as oxyethylene chains (ε = 1 × 10^5 l mol^{-1} cm^{-1}),[12] oxyethylenealkoxy chains (ε = 2 × 10^5 l mol^{-1} cm^{-1})[26] or octadecyl chains (ε = 1.64 × 10^5 l mol^{-1} cm^{-1}).[27] These results indicate that the siloxane chains, particularly polymethylphenyl siloxane chains, have an effect on the optical absorption intensity of the phthalocyanines.

All of the silicone lead phthalocyanines, PbPc(Bu^{n}PDMS$_{10}$)$_4$, PbPc(Bu^{n}PDMS$_{19}$)$_4$ and PbPc(Bu^{n}PMPhS$_{10}$)$_4$ are isotropic viscous green liquids at room temperature. No birefringence is observed under crossed polarizers. The respective glass transition temperatures as determined by differential scanning calorimetry (DSC) measurements are −122 °C, −121 °C and −46 °C (Fig. 3). Similar glass transitions are measured for the phthalonitrile precursors (**6a–c**) indicating that the siloxane chains determine the liquid character of these materials. PDMS materials whether they be oligomeric, high molecular weight, cyclic or networked have a narrow Tg range (−120 to −125 °C) reflecting the high dynamic flexibility of the dimethylsilicone chain.[28] Substitution of a phenyl group for a methyl group in the siloxane polymer stiffens the siloxane chain and elevates the Tg and viscosity. The polymethylphenylsiloxane substituted phthalocyanine PbPc(Bu^{n}PMPhS$_{10}$)$_4$ is a more viscous material with higher Tg value (−46 °C) than PbPc(Bu^{n}PDMS$_{10}$)$_4$ and PbPc(Bu^{n}PDMS$_{19}$)$_4$. This trend in Tg values correlates well with the data reported in the literature for varying degrees of phenyl for methyl substitution in the PDMS chain.[29]

Refractive index and thermorefractive properties

The refractive index of each of the lead substituted siloxy phthalocyanines is measured with a prism coupling instrument. The temperature dependence of the refractive index of a thin film of PbPc(Bu^{n}PDMS$_{10}$)$_4$, is deduced from ellipsometric measurements and is shown in Fig. 4.[30] The refractive index derived from ellipsometry at 24 °C is within experimental error of that measured on the prism coupling instrument at 532 nm, 1064 nm, and 1550 nm. The measured refractive index at 1550 nm decreases from 1.492 to 1.465 over a temperature range of 24 to 95 °C. This corresponds to a dn/dT = −4 ± 1 × 10^{-4} °C^{-1}. The measured dn/dT is within experimental error of this value between 1100 nm and 1550 nm. In the regions of strong absorption, the variation of index with temperature is not simple partially due to the temperature dependence of the monomer–dimer equilibrium (see below).

The observed dn/dT of PbPc(Bu^{n}PDMS$_{10}$)$_4$ is close to the dn/dT reported (−4 × 10^{-4} °C^{-1}) for linear dimethylsiloxane

Fig. 2 Electronic spectra of PbPc(Bu^{n}PDMS$_{10}$)$_4$, PbPc(Bu^{n}PDMS$_{19}$)$_4$ and PbPc(Bu^{n}PMPhS$_{10}$)$_4$ in dilute toluene solutions.
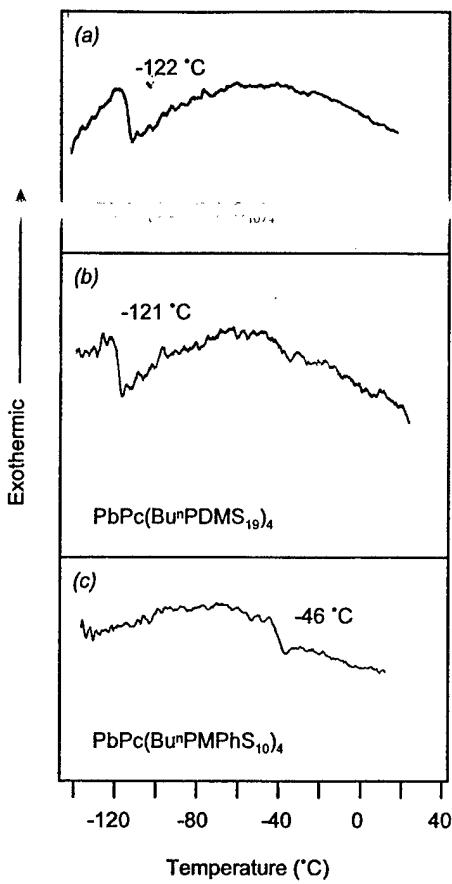
Fig. 3 Differential scanning calorimetry thermograms of PbPc-$(Bu^nPDMS_{10})_4$, $PbPc(Bu^nPDMS_{19})_4$ and $PbPc(Bu^nPMPhS_{10})_4$.
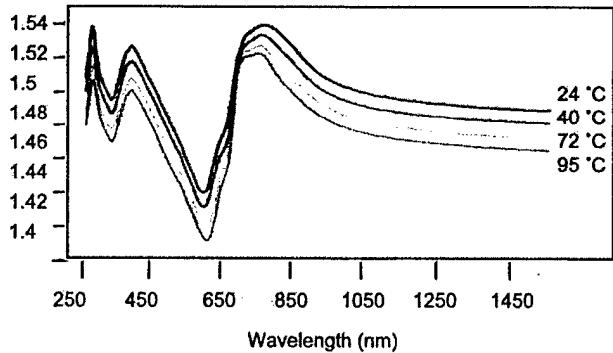
Fig. 4 Temperature dependence of the refractive index of $PbPc(Bu^n-PDMS_{10})_4$ as deduced from spectroscopic ellipsometry measurements.

oligomers alone.[8] The temperature dependence of the refractive index of silicone substituted phthalocyanines is apparently dominated by the PDMS chains. Polydimethylsiloxane has an exceptionally large dn/dT,[31] relative to other polymers. The observed dn/dT for the siloxy phthalocyanine demonstrates that we were successful at introducing the large siloxane dn/dT with a phthalocyanine chromophore.

The room temperature refractive indices for two different siloxy phthalocyanine compounds are shown in Table 1. $PbPc(Bu^nPMPhS_{10})_4$, with methylphenyl substitution shows a higher refractive index than the polydimethylsiloxane lead phthalocyanine, $PbPc(Bu^nPDMS_{10})_4$, at each of the measured wavelengths. This variation correlates with an expected effect of the phenyl group substituted in place of one of the methyl groups in the PDMS oligomer chain. Depending on the wavelength this refractive index variation ranges from 0.020 to 0.027. By comparison the refractive index variations for the

Table 1 Wavelength dependence of the refractive indices

Wavelength/nm	$PbPc(Bu^nPDMS_{10})_4$ refractive index	$PbPc(Bu^nPMPhS_{10})_4$ refractive index
1550	1.496	1.523
1319	1.500	1.527
1064	1.511	1.531

respective hydride and phthalonitrile terminated siloxane-oligomer analog precursors are 0.125 and 0.092 (see n_D 589 nm measurements in the Experimental section). While this comparison is not quantitative due to the difference of wavelength in the measured refractive indices, a qualitative effect of phthalonitrile termination and particularly phthalo-cyanine termination on diminishing this refractive index difference between the PDMS and PMPhS system is observed and is indicative of the large contribution of the phthalocya-nine ring polarizability to the refractive index of this material. However, the dn/dT is dominated by the siloxane oligomer as described above.

Aggregation studies

Aggregation is the association of the phthalocyanine molecules to form dimers, trimers and higher oligomers. The formation of coaxial stacks of the rings is easy to visualize. The rings can also be offset as far as side-by-side. For nonlinear optical appli-cations such as optical limiting, aggregation is of particular importance because the aggregates can have different optical properties from the monomer.[32] Various techniques have been used to study aggregation in solution including UV-Vis[33-35] and NMR[36] spectroscopy. Here, the concentration dependence of the UV-Vis spectra is used to examine the aggregation behavior of the polydimethylsiloxane lead phthalocyanines $PbPc(Bu^nPDMS_{10})_4$ and $PbPc(Bu^nPDMS_{19})_4$ as well as the metal free derivative $H_2Pc(Bu^nPDMS_{10})_4$.

Fig. 5 shows the concentration dependence of the observed molecular absorption coefficients for $PbPc(Bu^nPDMS_{10})_4$ in toluene solution. At low concentrations, the spectrum is dominated by the strong $\pi-\pi^*$ absorption of the monomer near 719 nm, usually called the Q-band. There is also a weaker vibronic satellite band at a shorter wavelength. As the concentration is increased, the apparent molar absorption coefficients of the monomer Q-band absorption decrease with the appearance of a species with a broader, overlapping absorbance to the red. The band to the red of the monomer Q-band can be assigned to the dimer. The appearance of an isosbestic point at 743 nm is consistent with a two-component equilibrium in the concentration range depicted in Fig. 5.
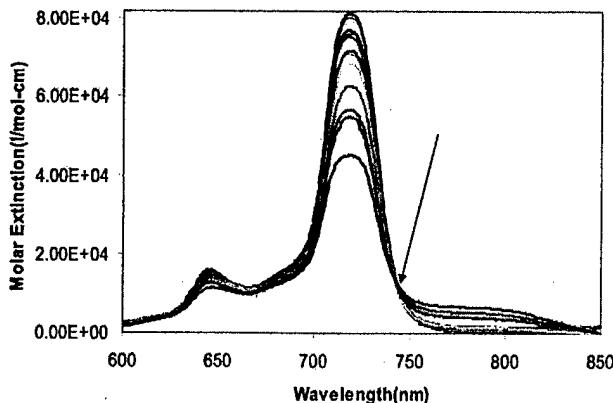

Fig. 5 Variation of the molar absorption coefficient of $PbPc(Bu^nPDMS_{10})_4$ in toluene as a function of concentration. The concentrations range from 6.2×10^{-7} M (top trace) to 4.7×10^{-2} M (lower trace). The arrow shows the location of the isosbestic point.

A simple monomer–dimer equilibrium model may apply over an appropriate concentration range with the attending basic equations for conservation of mass (eqn. 1), mass-action (eqn. 2) and additivity of optical absorbances (eqn. 3) used for the determination of the dimerization constant:[37]

$$Pc_1 + Pc_1 \overset{K_d}{\rightleftarrows} Pc_2 \tag{1}$$
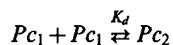
$$C_0 = [Pc_1] + 2[Pc_2] \quad x = \frac{[Pc_1]}{C_0} \quad 1 - x = \frac{2[Pc_2]}{C_0}$$

$$K_d = \frac{[Pc_2]}{[Pc_1]^2} = \frac{1-x}{2C_0x^2} \tag{2}$$

$$\varepsilon = \left(\frac{[Pc_1]}{C_0}\right)\varepsilon_1 + \left(\frac{2[Pc_2]}{C_0}\right)\varepsilon_2 = (\varepsilon_1 - \varepsilon_2)x + \varepsilon_2 \tag{3}$$

where K_d is the dimerization constant, C_0 is the analytical concentration of phthalocyanine, $[Pc_1]$ and $[Pc_2]$ are the respective equilibrium concentrations of phthalocyanine monomer and dimer, x is the mole fraction of phthalocyanine monomer, and ε is the observed analytical molar absorption coefficient per phthalocyanine structural unit, with ε_1 and ε_2 being the respective monomer and dimer molar absorption coefficients per phthalocyanine structural unit. In this work K_d is utilized as a measure of aggregation tendency. The data handling to determine K_d involves iterative plots of ε vs. x according to eqn. 3 wherein calculated values of x are obtained from the experimental values of C_0 and trial values of K_d according to eqn. 2. Of the various trial K_d values, the one that provides the best conformity with a straight line (maximum correlation coefficient determined by a plot of K_d vs correlation coefficient) is the one that best fits the data to the monomer–dimer equilibrium model. To determine that the concentration range is appropriate for this model, the data points corresponding to the most concentrated solutions are successively removed from the data set and the iterative determination of K_d redone until the K_d value becomes independent of concentration.

Fig. 6 depicts the concentration dependence of the Q-band molar absorption coefficient maxima for the PDMS lead phthalocyanines PbPc(Bu^{n}PDMS$_{10}$)$_4$ and PbPc(Bu^{n}PDMS$_{19}$)$_4$. A drop in the molar absorption coefficient indicates the onset of dimerization. The higher the concentration at which this occurs, the lower the aggregation tendency. The corresponding dimerization constants of the silicone phthalocyanine compounds are 2 M^{-1} for PbPc(Bu^{n}PDMS$_{10}$)$_4$ and 5 M^{-1} for PbPc(Bu^{n}PDMS$_{19}$)$_4$. For typical phthalocyanines compounds K_d ranges from 10^3 to 10^6 M^{-1}, depending on the peripheral group substituent, complexed metal ion, solvent and temperature.[37] The observed K_d values indicate a very small tendency for aggregate formation for these compounds. More specifically, the observed K_d values are significantly smaller than that observed for lead tetracumylphenoxy phthalocyanine (PbPc(CP)$_4$) which had an aggregation constant of 400 M^{-1}. Both PbPc(Bu^{n}PDMS$_{10}$)$_4$ and PbPc(Bu^{n}PDMS$_{19}$)$_4$ remain essentially monomeric in toluene up to concentrations of about 5 mM.

Molecular aggregation in the metal free derivative H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ was also studied. Fig. 6b shows the concentration dependence of the molar absorption coefficient of H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ at the peak of one component of the Q-band at 703 nm. A similar plot for the tetracumylphenoxy metal free phthalocyanine (H$_2$Pc(CP)$_4$), an example of a moderately aggregated phthalocyanine compound[15] is also shown for comparison. The effective molar absorption coefficient at the peak of the Q-band for H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ diminishes at higher concentrations than does the effective molar absorption coefficient for the comparable H$_2$Pc(CP)$_4$ solutions. H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ has a much weaker tendency to form aggregates than H$_2$Pc(CP)$_4$. Quantitatively, the dimerization
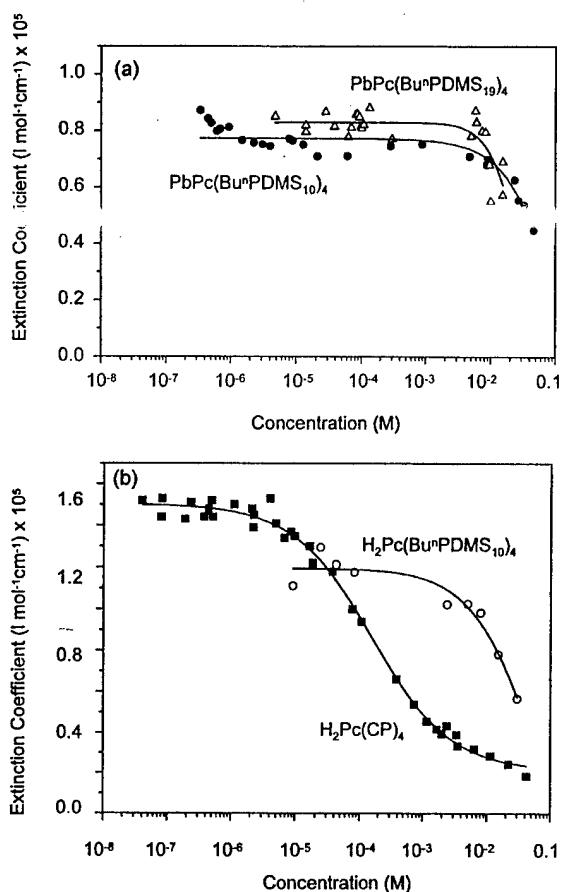

Fig. 6 Molar absorption coefficients at the Q-band maxima as a function of concentration for PbPc(Bu^{n}PDMS$_{10}$)$_4$, PbPc(Bu^{n}PDMS$_{19}$)$_4$, H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ and H$_2$Pc(CP)$_4$.

constant for H$_2$Pc(Bu^{n}PDMS$_{10}$)$_4$ was 31 M^{-1}, about a factor of 225 smaller than for H$_2$Pc(CP)$_4$ ($K_d = 7000 \pm 50$ M^{-1}). The aggregation constant of the metal free material is larger than for the lead phthalocyanine. This is consistent with other phthalocyanines where the introduction of a lead atom into the Pc cavity yields smaller aggregation constants.[21]

Fig. 7 shows a comparison of the molar absorption coefficient of a 0.033 M solution with that of the pure PbPc-(Bu^{n}PDMS$_{10}$)$_4$ (trace A) with the spectra of a 4 µm films of pure PbPc(Bu^{n}PDMS$_{10}$)$_4$ (trace B) and of PbPc(Bu^{n}PDMS$_{19}$)$_4$
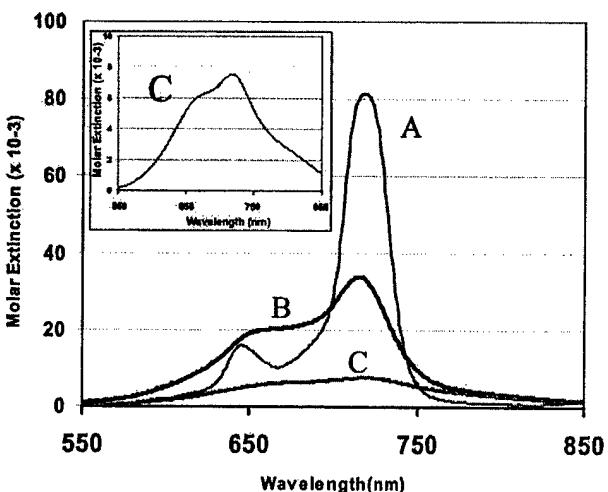

Fig. 7 Comparative electronic spectra for A) 0.033 M PbPc(Bu^n-PDMS$_{10}$)$_4$ in toluene to B) the pure material. Also shown is C) the molar absorption coefficient spectrum of pure PbPc(Bu^{n}PDMS$_{19}$)$_4$. The inset is C) on an expanded scale.

(trace C and the inset). The molar absorption coefficients of the pure materials were found by estimating the density of the pure materials. The spectral changes are distinctly different from those observed upon aggregation in solution displayed in Fig. 5. Comparing traces A and B, the Q-band near 715 nm for the pure material is broader. Also, there is a loss in integrated intensity and some evidence for an absorption near 680 nm, to

intermolecular interactions in the pure state different from aggregation observed in solution.

The most notable difference in the two thin film spectra in Fig. 7 is that the Q-band of pure PbPc(Bu″PDMS$_{19}$)$_4$ is considerably less intense than that of pure PbPc(Bu″PDMS$_{10}$)$_4$. We saw in Fig. 2 that in dilute solution, the molar absorption coefficients of PbPc(Bu″PDMS$_{10}$)$_4$ and PbPc(Bu″PDMS$_{19}$)$_4$ are similar, so the difference is characteristic of the pure material. The peak absorption is shifted very little, but the integrated absorption coefficient is a little smaller in PbPc(Bu″PDMS$_{10}$)$_4$. However, the Q-band absorption of pure PbPc(Bu″PDMS$_{19}$)$_4$ is a factor of 4.5 weaker than that of PbPc(Bu″PDMS$_{10}$)$_4$ and more than an order of magnitude less intense than the same material in dilute solution.

The origin of the decrease in the molar absorption coefficients of the Q-bands in the pure PbPc(Bu″PDMS$_{19}$)$_4$ material is not obvious. The small equilibrium constants for dimerization in toluene demonstrate that the polydimethyl-siloxane substitution is very effective at reducing the tendency of the phthalocyanines to aggregate. It seems unlikely that increasing the length of the siloxy chains in going from compound PbPc(Bu″PDMS$_{10}$)$_4$ to PbPc(Bu″PDMS$_{19}$)$_4$ would increase the tendency to aggregate. If the decrease in molar absorption coefficient is due to aggregation, the structure of the aggregate in the pure material may be different from that in toluene solution.

Different geometries for the aggregates are suggested by the observation that in toluene solution, the dimer absorption band is to the red of the monomeric Q-band, whereas in the pure material, the aggregate absorption is mainly to the blue. The spectral shift upon aggregation is related to the exciton splitting in the dimer, which, in turn depends on the aggregate structure. The shift is proportional to[38]

$$M^2 \frac{(1 - 3\cos^2\theta)}{R^3} \quad (4)$$

where M is the transition dipole of the phthalocyanine, θ is the angle between the transition dipole of the two adjacent molecules in the dimer with respect to the axis through the centers of the molecule and R is the distance between the centers of the molecule. The observed shift between the monomer Q-band and dimer in toluene compared to that in the pure material could imply that in toluene, the phthalocyanine rings aggregate with the rings offset, i.e. the angle between the centers of the rings is greater than 57 degrees, whereas in the pure material, this angle is smaller and the rings are closer to vertically stacked. Such different spectral shifts have been reported for two similar phthalocyanines that pack differently: i.e. a blue shift for vertically stacked rings and a red shift for a side-by-side configuration.[39] While the spectra are consistent with different dimer structures, it is also possible that the differences in the observed spectra arise for other reasons, such as multiple dimeric structures.

Nonlinear optical properties

As noted above, the principal motivation for the synthesis of the polydimethylsiloxane lead phthalocyanines PbPc(Bu″PDMS$_{10}$)$_4$ and PbPc(Bu″PDMS$_{19}$)$_4$, was to examine their potential for nonlinear optical applications including optical limiting. The Pb phthalocyanine chromophore is a very efficient nonlinear absorber and the isotropic liquid character of the pure material

enables the preparation of nonscattering thin films of high optical quality. Here we evaluate the potential of the pure lead polydimethylsiloxane phthalocyanine films for such applications. More detailed studies of the nonlinear optical properties are in progress.

In order to verify that these materials were nonlinear absorbers (reverse saturable absorbers) picosecond time-

these experiments, the sample is excited at 606 nm and the absorption spectrum is recorded with a continuum probe before and at several times after the sample is excited. Representative transient absorption spectra of PbPc(Bu″PDMS$_{10}$) are shown Fig. 8. At negative time, when the continuum probe pulse arrives before the excitation pulse, the plot of change in optical density (delta OD) with wavelength is flat indicating that there is no change in the observed absorption spectrum. The trace at 20 ps after excitation shows that there is an immediate appearance of a broad region of induced absorption. This is a direct measurement of the spectral region over which the excited state absorption coefficients exceed those of the ground state. The breadth of this region is comparable to that observed in other PbPcs[1,2] and several InPcs.[3] The other two traces in the figure show that this induced absorption remains strong at 493 ps and at 1160 ps after excitation. The 500 nm to 600 nm spectral region shows little change for at least 1.2 ns after excitation. The apparent excited state lifetime for the carrier of the absorption in this region is longer than 2.5 ns. Estimates of the excited state cross sections from this data indicate that they are comparable to those observed for other PbPcs and InPcs.[1-3] Between 440 and 500 nm the induced absorption increases from 3 ps to 0.5 ns and then decays somewhat between 0.5 and 1.2 ns. The origin of this spectral evolution is not fully understood but may be due either to participation of multiple excited states or may have to do with conformational changes of the bulky peripheral polydimethyl-siloxane chains.

Picosecond time resolved degenerate four-wave mixing (DFWM) experiments verify that the excited state lifetime is longer that 5 ns. Fig. 9 shows time resolved DFWM data obtained from a grating excited by orthogonally polarized 606 nm pump pulses. An immediate rise of the signal is apparent. More importantly the signal does not appreciably decay over the 1.2 ns duration of the experiment. Neither excited state nor chromophore reorientational mechanisms decay on this time scale. This confirms that the lifetime for the induced absorption in this region is much longer than 5 ns. In contrast, the metal free siloxy Pc, H$_2$Pc(Bu″PDMS$_{10}$)$_4$, has a lifetime measured to be 100 ps. The short excited state lifetime of
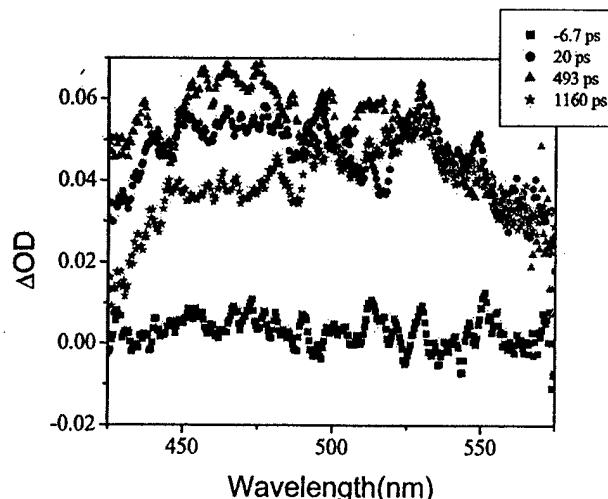

Fig. 8 Transient absorption spectra of PbPc(Bu″PDMS$_{10}$)$_4$. The legend shows the time after excitation.
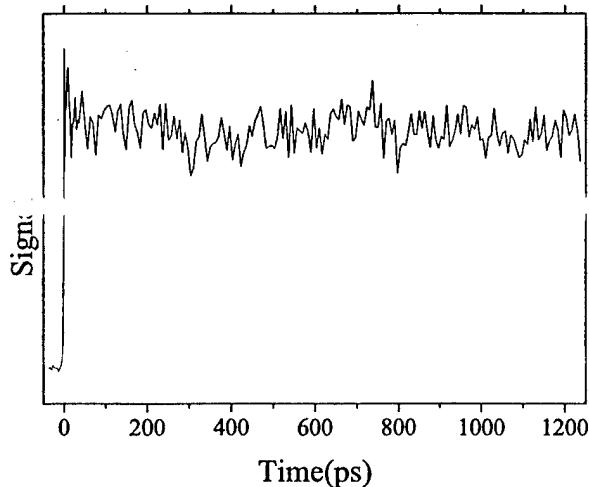
Fig. 9 Degenerate four-wave mixing signal from PbPc(Bu"PDMS$_{10}$)$_4$. The grating is written with cross polarized laser beams at 606 nm.

H$_2$Pc(Bu"PDMS$_{10}$)$_4$ means it is practical as an optical limiter only for pulses shorter than 100 ps.

Nanosecond nonlinear absorption and optical limiting experiments were performed on thin films of the lead phthalocyanines PbPc(Bu"PDMS$_{10}$)$_4$ and PbPc(Bu"PDMS$_{19}$)$_4$ in cells with path lengths of 4.22 µm and 3.82 µm respectively. The liquid character made it possible to fill these short path length cells by capillary action.

The visible spectrum of the phthalocyanine films is shown in Fig. 7. The weak, relatively broad Q-band absorption in the PbPc(Bu"PDMS$_{19}$)$_4$ film is notable. This is partly because the molecular volume per chromophore is larger in the PbPc-(Bu"PDMS$_{19}$)$_4$, because of the long peripheral groups, but even when normalized for the concentration, the absorption coefficient of the Q-band in the pure thin film is more than an order of magnitude smaller. The absorption coefficient of PbPc(Bu"PDMS$_{19}$)$_4$ was sufficiently small that it was also possible to perform nonlinear absorption experiments in a cell with a path length of 48.2 µm.

The nonlinear transmission and optical limiting curves for compound PbPc(Bu"PDMS$_{10}$)$_4$ taken at 532 nm are compared in Fig. 10. The difference between the experiments is that nonlinear transmission is measured with collection optics such that all of the light is collected while optical limiting is measured with an f/5 aperture inserted before the collection lens. Nonlinear transmission experiments measure only the
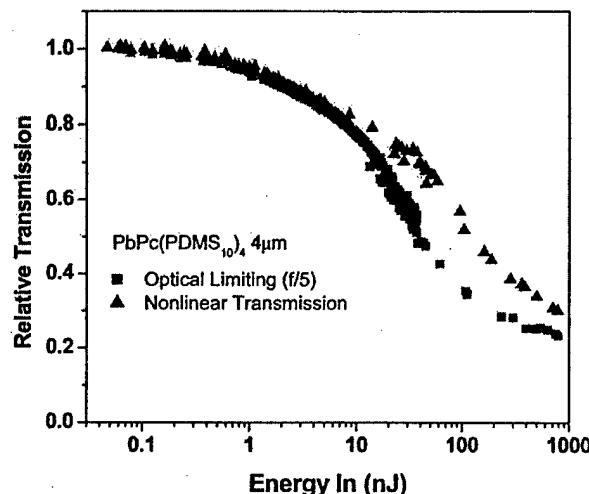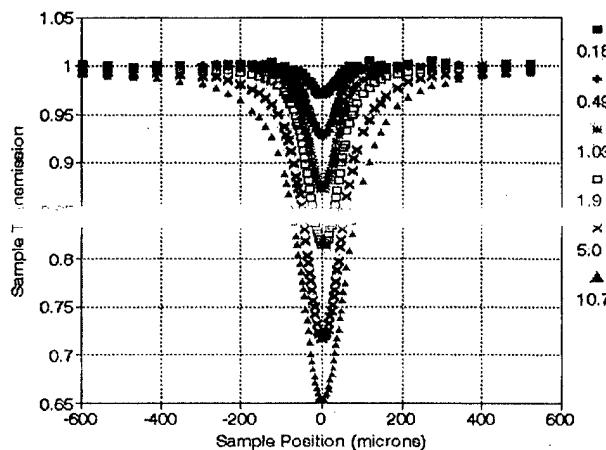

Fig. 11 Open aperture z-scans for PbPc(Bu"PDMS$_{19}$)$_4$ at 532 nm. The legend indicates the relative fluence for each trace in the experiment.

absorptive part of the response while the optical limiting experiments have contributions from both refractive and absorptive responses. The results show that at low excitation energies both curves are superimposable; nonlinear absorption dominates the low fluence response. At excitation energies above 10 nJ the two curves deviate with the optical limiting experiment reaching lower transmittances than the nonlinear transmission. The threshold for optical limiting where $T(I)/T_0$ = 0.5 is 25 nJ which compares to 8 nJ observed for a chloroform solution of PbPc(CP)$_4$.[1] The high fluence behavior shows that refractive mechanisms significantly contribute to the optical limiting response consistent with the large values of dn/dT discussed above. Similar data is observed from cells containing pure PbPc(Bu"PDMS$_{19}$)$_4$. In addition, there was evidence for higher order nonlinear absorption processes contributing to the nonlinear absorption in this material.

To examine the nonlinear refractive response in PbPc(Bu"PDMS$_{19}$)$_4$, a series of z-scans were carried out at different excitation energies. Fig. 11 shows the open aperture results. These results are typical of a strong nonlinear absorber. Fig. 12 shows the results from derived from closed aperture z-scans where the nonlinear absorption contribution has been removed and hence shows only the refractive part of the response. At low excitation energies the data show the signature of a positive refractive component. The refractive index of the excited state is greater than that of the ground state. At higher excitation energies, the shape of the z-scan trace becomes more complex, with evidence of an increasingly strong negative refractive response building in with increasing

Fig. 10 Optical limiting and nonlinear transmission measurements for PbPc(Bu"PDMS$_{10}$)$_4$ at 532 nm.
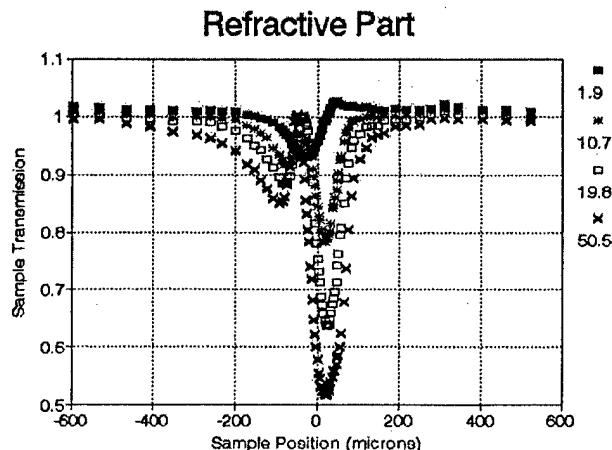

Fig. 12 Refractive component deduced from the closed aperture z-scans for PbPc(Bu"PDMS$_{19}$)$_4$ at 532 nm. The legend indicates the relative fluence for each trace in the experiment.

fluence. The negative sign of this second component of the response is consistent with the expected thermorefractive response superimposed on the excited state response. It is also consistent with the large d*n*/d*T* coefficient measured in static experiments above. The different z dependence of the two components of the refractive response has been observed previously. It is consistent with a thermal nonlinearity giving response.[3,40] We conclude that the enhancement in the optical limiting response seen in Fig. 10 at high fluences is largely due to the thermal response of the PDMS side chains.

Conclusions

This paper has described the synthesis and characterization of three polysiloxane substituted lead phthalocyanines. These new materials are isotropic liquids at room temperature that combine desirable optical properties of the phthalocyanines with those of the siloxanes in a single material. The variation of the refractive index with temperature indicates a large negative thermorefractive coefficient similar in magnitude to that observed from neat siloxanes. Measurements of the variation of the molar absorption coefficient as a function of concentration show that there is little evidence of aggregation in toluene solutions and only a small degree of aggregation in the neat liquid. The spectra at high concentrations in toluene compared to that in pure materials indicate that the structure of the aggregate in toluene could differ from that of the pure material.

Transient absorption studies of the neat liquid lead substituted materials show a broad spectral region of induced absorption similar to that observed from other lead phthalocyanines. That broad region of induced absorption persists for at least many nanoseconds. DFWM studies verify that the excited state lifetime is long compared to nanosecond pulses used to do optical limiting. Nonlinear transmission, optical limiting and z-scan results show that these siloxy materials possess a nonlinear absorption coefficient similar to that found in other lead substituted phthalocyanines. The nonlinear response has the additional feature of a large thermal nonlinear refractive response that contributes strongly to optical limiting at high fluence.

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